11 PHASE EQUILIBRIA

In the previous chapter equilibria in heterogeneous systems, such as liquid - vapour, solid - liquid etc. have been discussed in terms of the kinetic theory and from the view point of thermodynamics. Since heterogeneous equilibria exist between two or more different phases, these are also known as *phase equilibria*. The conditions of equilibria between the various phases of a substance can be represented simultaneously on a single graph which is known as a *phase diagram*. Heterogeneous equilibria or phase equilibria may also be described in terms of a very important and exact generalization known as the *phase rule*. The rule is based purely on thermodynamics and is applicable to all macroscopic systems involving heterogeneous equilirbria. It is independent of atomic or molecular structure. When properly applied to systems at true equilibria, the rule gives clearly and unequivocally the maximum number of phases that can co-exist under a set of conditions and puts a limit to the variables of the systems such as temperature, pressure, concentration etc. It does not, however, consider the effect of gravitation, electrical and magnetic fields and surface forces. The rule also does not say anything about the time required for a certain reaction to be complete or the time required for the attainment of equilibrium. The phase rule, discovered by William Gibbs(1874), can be mathematically stated as follows :

$$F = C - P + 2$$

where F is the number of *degrees of freedom,* C is the number of *components* and P is the number of *phases.*

If a small quantity of a volatile liquid is introduced in the Torricellian vacuum, the liquid passes to the vapour phase and exerts a pressure causing a depression of mercury meniscus (*Section 3.1* and Figure 3.1). When sufficient liquid is introduced, a heterogeneous equilibrium between liquid and vapour is established and the liquid exerts a definite vapour pressure at a definite temperature. Two important conclusions can be drawn:

(i) The pressure exerted is a function of the quantity of the liquid up to a certain limiting quantity of the liquid and

(ii) The pressure is independent of the quantity of liquid after the limit has been exceeded and is called the *saturated vapour pressure* of the liquid. In the latter case only temperature influences the vapour pressure.

Thus in the unsaturated state vapour will obey the gas laws but in the saturated case involving heterogeneous system at equilibrium, the pressure will be governed by the Clausius-Clapeyron equation (*Section7.15*).

11.1 Definition of Terms

Before describing the phase rule and applying it to specific systems, three terms must be defined and explained. The meaning and significance of these terms, (i) *phase,* (ii) *component* and *(iii) degrees of freedom,* are to be thoroughly understood as a prerequisite to the study of phase rule.

(i) Phase (*P*): A phase may be defined as :

The homogeneous part of a heterogeneous system which is physically and chemically different from other parts of the same system and bounded by surfaces of separation and mechanically separable.

A system can consist of one or more phases. Some examples are given below:

One phase systems:

(a) *A pure substance in one physical state.*

(b) *A mixture of liquids which are completely miscible with each other in all proportions is one phase in the liquid state, e.g.,* H_2O/*Alcohol etc.*

(c) *A pure gas or a mixture of gases which do not react with each other.*

(d) *A solution of a solid in a liquid,* $NaCl/H_2O$, *Sugar*/H_2O *etc.*

(e) *A mixture of solids in the molten state.*

Two phase systems:

(a) *A pair of immiscible liquids, e.g.,* CCl_4/H_2O, $C_2H_2Cl_2/H_2O$, *etc.*

(b) *A liquid and its vapour.*

(c) *A solid substance and its liquid phase or vapour phase.*

(d) *A mixture of solids in the liquid (molten) phase and one of the solids in the solid phase.*

(e) *A mixture of two solids which do not react with each other.*

Three phase systems:

(a) *A pure substance existing in three phases together, e.g. ice, water and water vapour*

(b) *A solid in two allotropic forms and the liquid mixture or in vapour phase.*

(c) *A mixture of two solids in the molten form and the two solids.*

(ii) **Component** (*C*)**:** The number of component is defined as

The minimum number of independently variable chemical entities required to describe all parts of a system

These chemical entities may undergo chemical reaction or physical changes or both, with an increase or decrease of different entities; the number of phases may also change depending on the nature of the changes. To define the equilibrium conditions of the system it will not be necessary to consider all the chemical entities. There can be systems of one, two or more components. Few examples are given below :

One component systems:

(a) *Water:* Water may exist in three different phases, solid, liquid and vapour. In each case the chemical entity is H_2O.

(b) *Sulphur:* Sulphur can exist in four phases – two allotropes (a) monoclinic (s), and (b) rhombic (s), as a liquid and as vapour. Again in all these phases the chemical constituent is the same.

Two component systems:

(a) If $CaCO_3$ is heated in a closed container it undergoes dissociation forming CaO and CO_2. When the system attains equilibrium all three chemical substances are present. These three chemical entities are related by the equation

$$CaCO_3(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

There will be three phases, each of the chemical entities representing a phase as they are bounded by a separate boundary, but *the number of components will be* **two** because all the three phases can be described by mentioning any two of them as they are related by the above equation.

(b) A solution of $NaCl$ is a one phase system. The *number of components* in the system is, however, two as the concentration can vary and the composition of the system cannot be described by mentioning any one of them. Similarly *the number of components* in a saturated solution of the salt is also two for the same reason.

(c) Systems in which salts form one or more hydrates are two component systems as the composition of all phases (hydrates) and water can be described by the constituents, e.g. the salt and water.

(d) Pairs of partly miscible or immiscible liquids.

(e) Pairs of metals which are miscible in the liquid phase but form separate pure solid metal phases.

(iii) **Degrees of Freedom** (F): The number of degrees of freedom (or variance) may be defined as,

The number of independent variables e.g, temperature, pressure and composition, which must be fixed in order to define the system completely.

A system with $F = 2$ is called bivariant
A system with $F = 1$ is called univariant
A system with $F = 0$ is called invariant

Three examples are :

(a) *A gaseous system :* The temperature, pressure and volume of a gas are related by an equation of state, $PV = RT$. The state of the gaseous system is completely defined by any two of the three variables.The third is automatically fixed. This is a *bivariant* system, i.e., the degree of freedom is two.

since at any temperature p_{Cao} and p_{CaCO_3} are considered to be constant. The value of the equilibrium constant at any temperature is determined solely by the equilibrium pressure of carbon dioxide evolved. This has been proved by experiments.

If, however, two or more gaseous substances are involved in the reaction the situation becomes complicated. For example, for the dissociation of solid ammonium hydrogen sulphide according to the equation

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

the equilibrium constant, K_p, is

$$K_p = p_{NH_3} \times p_{H_2S} \tag{10.17}$$

Here the equilibrium constant is the product of the partial pressure of ammonia and hydrogen sulphide gas. If the partial pressure of one of the two is increased, the partial pressure of the other must decrease so that K_p remains the same.

Evaporation of a liquid and sublimation of a solid may also be regarded as examples of heterogeneous equilibria in so far as more than one phase are existing together at equilibrium. Hence the vapour pressure of a liquid or a solid is one type of equilibrium constant. But these are physical equilibria.

Another type of physical equilibrium is a saturated solution in contact with the solute

$$Solid\ solute + aq \rightleftharpoons Saturated\ solution \tag{10.18}$$

The equilibrium constant in its most correct form is

$$K' = \frac{a_{solution}}{a_{solute}} \tag{10.19}$$

where a stands for activity. The solute being solid its activity is taken as unity so that $K' = a_{solution}$. As the solution is saturated $a_{solution}$ at the temperature may be replaced by solubility, S, and we obtain

$$K = Solubility(S) \tag{10.20}$$

As will be seen in *Chapter 17*, important information may be derived with the help of these deductions.

10.12 Factors Influencing Equilibrium: The Principle of Le Chatelier

A chemical reaction at equilibrium will maintain this condition indefinitely unless disturbed by changes from outside. Factors which may cause such disturbances are

(a) a change in concentration of any of the species present at equilibrium,

(b) a change in pressure in the case of equilibria where gases are present,

(c) change in temperature of the reaction, or

(d) addition of an inert substance.

The effect of these changes on the position of chemical equilibrium was qualitatively summarized by what is known *as the principle of Le Chatelier*. The principle states that

'When a system is at equilibrium, a change in any one of the factors upon which the equilibrium depends will cause the equilibrium to shift in a direction such that the effect of the change is diminished'. Alternatively,

'If a stress is applied to a system at equilibrium, the position of equilibrium shifts in such a way that the effect of the stress is minimized.'

The resulting system will, however, be still in equilibrium unless the change is very large. ***Equilibrium constant depends only on temperature but remains unchanged if any of the other factors is changed***. The principle is of general utility and may also be applied to physical equilibria. This principle is also known as *the principle of mobile equilibrium*, clearly indicating that the equilibrium position can be easily shifted by changing conditions of the reaction. The equilibrium may be shifted to the right (product side) or to the left (reactant side), the direction of the change depending on the nature of the change brought into the system by altering the conditions that govern the equilibrium.

10.12.1 Effect of change in concentration

Let us consider the equilibrium position for the dissociation of phosphorous pentachloride to phosphorous trichloride and chlorine:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If to the system at equilibrium some chlorine is added the concentration of chlorine increases. According to Le Chatelier principle the system tries to diminish the effect of added chlorine. This is possible if the added chlorine is used up by combining with phosphorous trichloride until a new equilibrium is reached. This means that the equilibrium shifts to the left forming some phosphorous pentachloride. Same thing happens if some phosphorous trichloride is added to the above equilibrium system. If, on the other hand, some phosphorous pentachloride is added to the equilibrium system the equilibrium will shift to the right.

The same conclusion can be arrived at by using the value of the equilibrium constant. At a given temperature the equilibrium constant for a particular reaction has a definite value even though one may start with different initial concentrations of either the reactants or products. Data in Table 10.1 confirm this statement. The value of the equilibrium constant will not change if to the system at equilibrium some additional quantity of either the reactant or product is added. Considering the above equilibrium the equilibrium constant, K_c, is

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

If to the system at equilibrium some chlorine is added the concentration of chlorine increases. As the value of K_c remains constant the denominator must increase. This is achieved

19-B

if some chlorine combines with phosphorus trichloride to form phosphorus pentachloride, i.e., if the equilibrium shifts to the left. This is in accordance with Le Chatelier principle

Similarly, if some phosphorus pentachloride is added to this system at equilibrium, part of it dissociates so that by adjustment of concentrations the value of K_c is maintained constant.

10.12.2 Effect of pressure change on chemical equilibrium

Homogeneous reactions in solution or in solid state are not accompanied by appreciable change in volume but this is not always the case with reactions involving gases. According to the principle of Le Chatelier, an increase of pressure on a reaction involving a gas or gases should cause the equilibrium to shift in the direction which will result in a decrease in volume, because by doing so the effect of the pressure is diminished. The decrease in volume takes place if, as a result of the reaction, the number of gaseous moles is decreased. However, in reactions where there is no volume change, i.e., there is no change in the number of mole, pressure has no effect on the equilibrium. These general remarks may be illustrated with the following examples.

(a) For the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine, the equilibrium constant in terms of the degree of dissociation (*Section 10.9*) is given by

$$K_p = \frac{\alpha^2}{1-\alpha^2} \times P \qquad (10.21)$$

If pressure P is increased, the denominator in equation (10.21) must increase in order to keep K_p constant. This is possible if the degree of dissociation, decreases, i.e., if some phosphorus trichloride and chlorine combine to form back phosphorus pentachloride. Conversely, if P is decreased, the degree of dissociation must increase so as to keep K_p constant. For this reaction the expression for K_p contains P as there is a change in the number of moles in the gaseous phase.

(b) The expression for equilibrium constant in terms of partial pressures for the decomposition of hydrogen iodide into iodine and hydrogen is

$$K_p = \frac{p_{H_2} \times p_{I_2}}{(p_{HI})^2} = \frac{x^2}{(1-2x)^2}$$

It will be noticed that there is no residual P term in the expression for K_p and, therefore, a change in the value of P will have no effect on the point of equilibrium. This occurs because $\Delta n = 0$ as a result of the decomposition of a given amount of hydrogen iodide. For all such reactions where there is no change in volume during the reaction, the equilibrium constant is independent of pressure, or volume.

10.12.3 Effect of temperature on equilibrium

The effect of temperature on equilibrium depends on whether the reaction is exothermic or endothermic.

According to the principle of Le Chatelier, an increase of temperature will cause the equilibrium to move in the direction in which the effect of the temperature rise may be minimized. For this to happen the equilibrium moves in a direction in which heat is absorbed. In the case of an exothermic reaction equilibrium moves to the reactant side as in this direction the reaction is endothermic. In the case of endothermic reaction equilibrium moves to the product side as the added heat can be used up if more products are formed. Conversely, a decrease of temperature will shift an exothermic equilibrium to the right and an endothermic equilibrium to the left. These conclusions are illustrated below:

The synthesis of ammonia by the Haber-Bosch process is exothermic

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ}$$

As heat is evolved in this reaction, an increase of temperature will cause the equilibrium to shift to the left, i.e., the yield of ammonia will be decreased on increasing the temperature. Conversely, if the temperature is decreased more of the product will be formed and the equilibrium shifts to the right.

If a reaction is endothermic, as in the production of nitric oxide by the Birklende and Eide process

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +180.0 \text{ kJ}$$

an increase in temperature (addition of heat) increases the amount of the product while cooling (removal of heat) decreases the amount of product, i.e., shifts the equilibrium towards the left.

The change of equilibrium constant with temperature may be expressed quantitatively (*Section 7.17*) in the form of the equation

$$\log K_p = -\frac{\Delta H}{2.303RT} + \text{constant} \tag{10.22}$$

where ΔH is the enthalpy change of the reaction. If ΔH is constant, a plot of $\log K_p$ *vs* $1/T$ gives a straight line whose slope is $\Delta H/(2.303\ R)$. A schematic representative plot is given in Figure 10.2. If ΔH is positive the slope is negative, while if ΔH is negative the slope is positive.

Hence for an exothermic reaction K_p decreases with increase of temperature, while for an endothermic reaction it increases with a rise in temperature. This is in agreement with Le Chatelier principle.

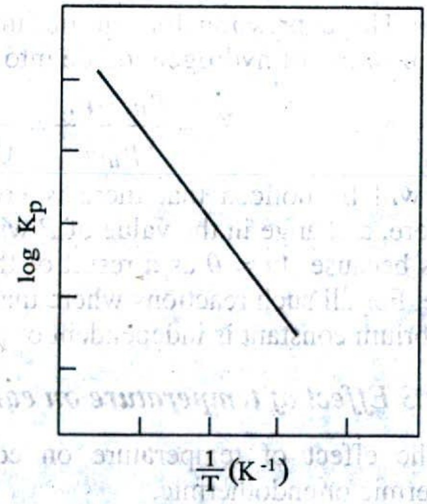


Figure 10.2 Plot of $\log K_p$ *vs* $\frac{1}{T}$ (endothermic reaction).

As pointed out earlier the vapour pressure of a liquid or solid and solubility of a substance in a solvent may be regarded as equilibrium constants. The effect of temperature on vapour pressure (p) and solubility (S) may be represented by similar equations, e.g.,

$$\log p = -\frac{\Delta H_{vap}}{2.303RT} + \text{constant} \tag{10.23}$$

$$\log S = -\frac{\Delta H_{solution}}{2.303\,RT} + \text{constant} \tag{10.24}$$

Equation (10.23) is one of the forms of Clausius-Clapeyron equation. If the enthalpy of reaction is known it is possible to calculate an equilibrium constant K_2 at temperature T_2 from the known value of K_1 at temperature T_1 from the following relationship:

$$\log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{10.25}$$

$$= -\frac{\Delta H}{2.303R}\left(\frac{T_1-T_2}{T_1T_2}\right) \tag{10.26}$$

Example 10.13: The equilibrium constant for the synthesis of NH_3 by Haber-Bosch process is 1.65×10^{-4} at 673 K. What will be the equilibrium constant at 773 K if the enthalpy of reaction is – 105.20 kJ?

Solution: According to equation (10.26),

$$\log \frac{K_{773}}{K_{673}} = -\frac{\Delta H}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\log K_{773} - \log(1.65\times10^{-4}) = -\frac{-105.20\times10^3}{2.303\times8.314}\left(\frac{1}{773}-\frac{1}{673}\right)$$

$$= -1.056$$

or, $\log K_{773} = -1.056 + \log(1.65\times10^{-4})$

$= -4.839$

Hence $K_{773} = 1.45\times10^{-5}$

10.12.4 Effect of adding an inert gas

If an inert (non-reacting) gas is added to a system of gaseous equilibrium at constant volume (the total pressure will increase), the equilibrium is not affected. This follows from Dalton's law of partial pressures, because according to this law the presence of a foreign inert gas in a closed space does not influence the partial pressure exerted by the reacting substances. This is true whether the reaction involves a change in the number of molecules or not. If, however, the pressure is kept constant while the inert gas is added to the system at equilibrium, (there is a consequent increase in volume), the equilibrium *is* displaced, according to the Le Chatelier principle, in cases of reactions where K_p is dependent on pressure. If K_p is independent of pressure, as in the decomposition of hydrogen iodide, there is no effect.

10.12.5 Effect of catalyst on equilibrium

A catalyst does not affect the position of equilibrium and hence it does not have any effect on the value of equilibrium constant of a reaction. This is because a catalyst affects the forward and reverse reaction equally.

10.13 Applications of the Principles of Chemical Equilibrium to Reactions of Industrial Importance

In industrial processes the primary objective is to maximize the yield of products at a minimum cost in a shorter period of time. To attain this objective in the case of gaseous reactions of industrial importance advantage is taken of the influence of pressure and temperature on the equilibrium yield of the desired product. These points will be illustrated with the help of a few industrially important reactions.

10.13.1 Synthesis of ammonia

The synthesis of ammonia on a commercial scale by the Haber-Bosch process is based on following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta H_{291} = -92.0 \text{ kJ}$$

$$\Delta H_{924} = -111.2 \text{ kJ}$$

For the calculation of the equilibrium constant, let the concentration (mol L^{-1}) of the various species at equilibrium be as follows:

	$N_2(g)$ +	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial (mol L^{-1})	1	3	0
Change	$-x$	$-3x$	$+2x$
Equilibrium	$1-x$	$3(1-x)$	$2x$

Hence $$K_c = \frac{(2x)^2}{(1-x)(3-3x)^3}$$

Total number of moles at equilibrium $= 1 - x + 3(1-x) + 2x = 4 - 2x$

where x is the number of moles of N_2 reacted. Let the equilibrium pressure be P atmosphere. The mole fractions of the components are :

$$x_{N_2} = \frac{1-x}{4-2x}; \quad x_{H_2} = \frac{3-3x}{4-2x} \text{ and } x_{NH_3} = \frac{2x}{4-2x}$$

Partial pressures $p_{N_2} = \frac{1-x}{4-2x} \times P;\ p_{H_2} = \frac{3-3x}{4-2x} \times P$ and $p_{NH_3} = \frac{2x}{4-2x} \times P$

or $p_{N_2} = \frac{1-x}{2(2-x)} \times P;\ p_{H_2} = \frac{3(1-x)}{2(2-x)} \times P$ and $p_{NH_3} = \frac{2x}{2(2-x)} \times P$

So,
$$K_p = \frac{p^2_{NH_3}}{p^3_{H_2} \times p_{N_2}} = \frac{\left(\frac{2x}{2(2-x)}\right)^2 \times P^2}{\left(\frac{1-x}{2(2-x)}\right) \times P \left(\frac{3(1-x)}{2(2-x)}\right)^3 \times P^3}$$

$$= \frac{16}{27} \cdot \frac{x^2(2-x)^2}{(1-x)^4 P^2} \qquad (10.27)$$

If x is small in comparison to unity, this reduces to

$$K_p = \frac{64x^2}{27P^2}$$

Or
$$x^2 = \frac{27}{64} K_p \times P^2 \qquad (10.28)$$

The reaction is a highly exothermic one and as equation (10.28) shows the equilibrium yield of ammonia depends on the pressure to a large extent. The suitable reaction conditions are low temperatures and high pressures. Some of the experimental results for this reaction are shown in Figure 10.3.

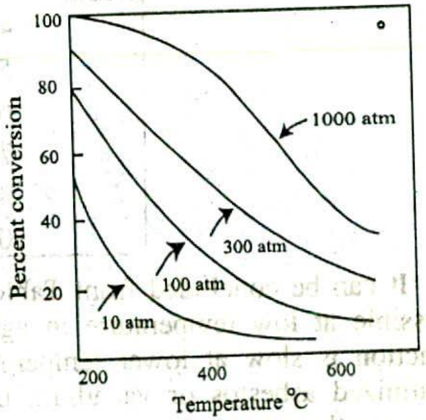


Figure 10.3 Yield of ammonia at different temperatures and pressures

At low temperature, however, the reaction is slow and the time to attain the desired yield is long. For the process to be economical the reaction should be conducted at the lowest temperature at which the reaction would proceed at the desired speed. In such industrial processes advantage is taken of the catalytic effect (see *Chapter 13)* of certain substances in increasing the speed of reaction. Iron with the addition of small amounts of the oxides of aluminum and potassium acts as good catalyst. For all catalytic reactions there is an optimum temperature at which the rate is such that the yield of the product is best for the cost involved.

As the reaction involves a decrease of volume, the yield of ammonia increases with increase of pressure. In the actual manufacturing process by the Haber-Bosch process a pressure of about 200 atm and temperature of about 450° to 550°C are used. In other modifications of the process, pressure as high as 1000 atmosphere is used.

10.13.2 *Formation of sulphur trioxide for the manufacture of sulphuric acid by the contact process*

An essential step in the manufacture of sulphuric acid is the oxidation of sulphur dioxide to sulphur trioxide according to the following exothermic reaction:

$$SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g) \qquad \Delta H = -96.0\ kJ$$

The equilibrium constant for this reaction in terms of partial pressures may be expressed as

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times p_{O_2}^{1/2}} \tag{10.29}$$

Some experimental values of K_p based on partial pressures in atmospheres are given in Table 10.2.

Table 10.2 Equilibrium constants for the reaction

$SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g)$ at different temperatures

Temperature (°C)	K_p
400	397.0
500	48.1
600	9.53
700	2.63
800	0.915
1000	0.185

It can be concluded from Table 10.2 that high conversion of $SO_2(g)$ into $SO_3(g)$ is possible at low temperature in agreement with Le Chatelier principle. However, the reaction is slow at lower temperatures. So for economic reasons a catalyst, such as platinized asbestos or vanadium pentoxide admixed with other materials, is used to increase the rate of the reaction. In the above reaction the number of moles of products is less than that of the reactants. Therefore, an increase of pressure would shift the equilibrium to the right, i.e. should lead to an increase in the yield of sulphur trioxide. However, as the yield at 1 atmosphere pressure and at temperatures between 400 – 450°C in the presence of the catalyst is about 97%, the reaction is carried out at a pressure of 1 to 2 atmosphere at a temperature of 400 – 450°C when the conversion is optimum.

10.14 Free Energy Change and Equilibrium Constant

We already know (*Section 7.12.2*) that the thermodynamic criterion for a chemical reaction at equilibrium is $(\Delta G)_{T,P} = 0$. This conclusion enables us to derive thermodynamically the relation between the equilibrium concentrations of reactants and products. Physical equilibria may also be described with the help of this criterion.

Let us consider a reaction involving four gases *A, B, K* and *L*

$$aA(g) \ + \ bB(g) \rightleftharpoons \ kK(g) \ + \ lL(g)$$

where a, *b*, *k* and *l* are the number of moles of the reactants and products as shown in the stoichiometric equation. For one mole of an ideal gas if the pressure is changed from P_1 to P_2 the difference in free energy is given by (*Section* 5.40)

$$G_2 - G_1 = RT \ln \frac{P_2}{P_1} \tag{10.30}$$

If $P_1 = 1$ atmosphere, i.e., the gas is in its standard state, then $G_1 = G° =$ free energy of the gas at its standard state. Hence it follows from equation (10.30) that

Free energy of *a* moles of $A = aG_A = aG°_A + aRT \ln p_A$ (10.31a)

Free energy of *b* moles of $B = bG_B = bG°_B + bRT \ln p_B$ (10.31b)

Free energy of *k* moles of $K = kG_K = kG°_K + kRT \ln p_K$ (10.31c)

Free energy of *l* moles of $L = lG_L = lG°_L + lRT \ln p_L$ (10.31d)

In these equations p_A, p_B, p_K and p_L are the pressures of the species. The free energy change for the reaction is then given by

$$\begin{aligned} \Delta G &= G_{products} - G_{reactants} \\ &= kG_K + lG_L - aG_A - bG_B \\ &= (kG°_K + lG°_L) - (aG°_A - bG°_B) + RT \ln \frac{(p_K)^k (p_L)^l}{(p_A)^a (p_B)^b} \end{aligned} \tag{10.32}$$

$$\Delta G = \Delta G° + RT \ \ln \frac{(p_K)^k (p_L)^l}{(p_A)^a (p_B)^b} \tag{10.33}$$

This relation gives free energy change of the reaction when the reactants at some arbitrary pressures, p_A and p_B, are converted into products at pressures, p_K and p_L, relative to the free energy change occurring when both reactants and products are in their standard states. In the special case when the reactants and products are in their standard states of 1 atmosphere, the term containing *P*'s vanish and ΔG is equal to $\Delta G°$ according to equation (10.33). When the system has reached equilibrium and the pressures are the equilibrium values $\Delta G_{\text{(reaction)}} = 0$ and equation (10.33) becomes

$$\Delta G° = -RT \ \ln \frac{(p_K)_e^k (p_L)_e^l}{(p_A)_e^a (p_B)_e^b} \tag{10.34}$$

But $$K_p = \frac{(p_K)_e^k (p_L)_e^l}{(p_A)_e^a (p_B)_e^b}$$

for the reaction at equilibrium. The subscript is added to indicate that the system is at equilibrium. Hence

$$\Delta G^\circ = -RT \ln K_p \tag{10.35}$$

Since ΔG° is constant, K_p must be a constant at a given temperature. This equation represents one of the most useful and important relation in thermodynamics. This relation enables one to calculate K_p for a reaction from the value of ΔG°. Conversely, if K_p can be determined the value of ΔG° may be calculated and hence the direction of chemical reaction may be predicted.

Expressions similar to equation (10.35) may be derived for other standard states. When the concentrations are expressed in mol L^{-1}, the equilibrium constant is related to standard free energy change by the relation

$$\Delta G^\circ = -RT \ln K_c \tag{10.36}$$

It must be noted that the value of ΔG^0 in equation (10.35) is not always the same as that of equation (10.36). The difference in the values of ΔG^o is due to choice of standard states.

Example 10.14: K_p for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ at 25°C is 0.14 atmosphere. Calculate the standard free energy change for this reaction. Will the reaction be spontaneous at this temperature?

Solution: $\Delta G^\circ = -RT \ln K_p = -(8.314)(298{\cdot}1)(2.303) \log 0.14$

$$= +4.85 \text{ kJ}$$

As ΔG^o is positive, the reaction will not be spontaneous and will not proceed without outside aid.

10.15 Influence of Temperature on Equilibrium Constant : Thermodynamic Derivation

Since K_p depends on temperature, differentiation of equation (10.35) with respect to temperature yields

$$-\frac{\partial(\Delta G^0)}{\partial T} = R \ln K_p + \frac{RT \partial \ln K_p}{\partial T} \tag{10.37}$$

When the reactants and products are in their standard states, the Gibbs–Helmholtz equation (*equation 7.74*) is written as

$$\Delta G^\circ = \Delta H^\circ + T\,\frac{\partial(\Delta G^0)}{\partial T} \tag{10.38}$$

Multiplying both sides of equation (10.37) by T we get

$$-T\frac{\partial(\Delta G^0)}{\partial T} = RT\ ln\ K_p + \frac{RT^2\partial\ln K_p}{\partial T} \tag{10.37a}$$

Substituting for $T\frac{\partial(\Delta G^0)}{\partial T}$ from equation (10.38) into equation (10.37a) yields

$$-(\Delta G^\circ - \Delta H^\circ) = RT\ ln\ K_p + \frac{RT^2\partial\ln K_p}{\partial T} \tag{10.38a}$$

Combining equations (10.35) and (10.38a) it follows that

$$\Delta H^\circ = \frac{RT^2\partial\ln K_p}{\partial T}$$

Rearrangement and use of ordinary differential gives

$$\frac{d\ ln\ K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{10.39}$$

This expression gives the relation between the equilibrium constant and temperature in the differential form and is known as the *van't Hoff reaction isochore*. This is a very important equation and may be used to determine heats of reaction from measurements of equilibrium constant of reactions. For this purpose more convenient forms are the integrated forms:

$$ln\ K_p = -\frac{\Delta H^0}{RT} + constant$$

and
$$ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{10.40}$$

to which references were made in *Section 10.12.3*.

Example 10.15: The equilibrium constant, K_c, of the reaction

$$Cyclohexane \rightleftharpoons Methylcyclopentane$$

at 25°C and 45°C are respectively 0.143 and 0.193. Calculate ΔH° for this reaction over this temperature range.

Solution: 25°C = 298 K and 45°C = 318 K

Using equation(10.40)

$$ln\frac{K_{318K}}{K_{298K}} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{318}-\frac{1}{298}\right]$$

$$\text{or} \qquad (2.303)\log\frac{0.193}{0.143} = -\frac{\Delta H^0}{(8.314)}\times\frac{298-318}{318\times298}$$

$$= +\frac{\Delta H^0}{(8.314)}\times\frac{20}{318\times298}$$

$$\therefore \qquad \Delta H^\circ = \frac{(8.314)(318)(298)(2.303)}{20}\log\frac{0.193}{0.143}$$

$$= 11.8 \text{ kJ mol}^{-1}$$

QUESTIONS AND PROBLEMS

1. What is a reversible reaction? Write expressions for the equilibrium constant K_c and K_p for the following reactions:
   (a) $2\,NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$
   (b) $2H_2S\,(g) + 3\,O_2\,(g) \rightleftharpoons 2H_2O(g) + 2SO_2(g)$
   (c) $4NH_3\,(g) + 5O_2\,(g) \rightleftharpoons 4NO\,(g) + 6H_2O\,(g)$
   (d) $NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$
   (e) $C\,(s) + 2N_2O\,(g) \rightleftharpoons CO_2\,(g) + 2N_2\,(g)$
   (f) $2NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g)$
2. In the case of the reaction: $3H_2\,(g) + N_2\,(g) \rightleftharpoons 2NH_3\,(g)$ write the expression for the equilibrium constant in terms of partial pressures.
3. Establish the relation between K_p and K_c. Explain, with the help of Le Chatelier's principle, the effect of pressure on the reaction :
   $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
4. Clearly explain your concept of dynamic equilibrium. What are the criteria of chemical equilibrium? At 49 °C and under a pressure of 4 atm., N_2O_4 is 63% dissociated into NO_2. Calculate the equilibrium constant.
5. What are the factors that influence chemical equilibrium? Explain with suitable examples the principle of Le Chatelier
6. For the reaction, $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ at equilibrium at 1000°K and 1.00 atm. total pressure the following mole fraction data were obtained :
   $SO_2 = 0{\cdot}309,\ SO_3 = 0{\cdot}338,\ O_2 = 0.353$
   Calculate the values of K_p and K_c stating the units in which they are expressed. Use the atmosphere and the litre as units of pressure and volume respectively.
   [Ans. $K_p = 0.295$ atm ; $K_c = 3{\cdot}60\times10^{-3}$ mol L^{-1}]
7. The dissociation constant for N_2O_4 at 8°C in chloroform solution is $1{\cdot}10\times10^{-5}$. If 0.40 mole of N_2O_4 is dissolved in 600 mL of chloroform solution, calculate (a) the concentration of NO_2 in the solution at equilibrium, and (b) the per cent dissociation of N_2O_4. [Ans. (a) 2.7×10^{-3} mol L^{-1} ; (b) 0.20 %]
8. Water expands when it freezes. Use the principle of Le Chatelier to predict the effect of pressure change on the freezing point of water.
9. The value of K_c for the reaction :
   $$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
   is 3.3×10^{-2} at 300 °C. Calculate the number of grams of HI formed when 1 mole each of hydrogen and iodine vapour and 0.001 mole of HI are allowed to come to equilibrium at this temperature in a 2 L flask. [Ans. 187 g]

10. At 400°C in an equilibrium mixture of nitrogen, hydrogen and ammonia the partial pressures are : p_{N_2} = 6.74 atm., p_{H_2} = 20.23 atm, p_{NH_3} = 3.03 atm. Calculate K_p for each of the following reactions at this temperature

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ [Ans. (a) 1.65×10^{-4} ; (b) 1.28×10^{-2}]

11. One mole of ethyl alcohol is mixed with 1 mole of ethanoic acid. At equilibrium at 25 °C it is found that 0.667 mole of ethyl acetate has been formed.

(a) Calculate the equilibrium constant for the reaction :

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(b) When 0.50 mole of ethanol is added to 1 mole of acetic acid how much ester will be formed at equilibrium? [Ans. (a) 4; (b) 0.422 g]

12. How may the equilibrium constant-temperature data be used to calculate the heat of reaction?

13. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the values of K_P at 25°C and 65°C are 0.141 and 2.80 respectively. Calculate the average heat of reaction. [Ans. 62.5 kJ]

14. A saturated solution of silver nitrite contains 3.40 g and 13.63 g of solute per 1000 g of water at 20 °C and 60 °C respectively. Calculate the mean heat of solution of the salt over this temperature range. [Ans. 28.2 kJ mol $^{-1}$]

15. The dissociation pressure of the system: $Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$ is 10.5 mm Hg at 340 °C and 101.2 mm at 421°C. Calculate the mean heat of dehydration over this temperature range. [Ans. –1001.9 J mol $^{-1}$]

16. Establish a relation between standard free energy change and the equilibrium constant of a reaction.

17. The ΔG^0 of the reaction is – 28.0 kJ :

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Calculate the value of K_p. [Ans. 1.02×10^5]

18. In the reaction :

$$3\,Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_{2(g)}$$

there is equilibrium at 200 °C when the partial pressure of steam is 46 mm Hg and that of H_2 is 960 mm Hg. Calculate the pressure of hydrogen when that of steam is 6.4 mm Hg. [Ans. 1338 mm Hg]

19. Phosphorus pentachloride when heated dissociates as follows: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ Calculate the equilibrium constant K_p of the reaction at 250 °C if 80% is dissociated when the total pressure is 1.00 atmosphere.

20. At 30°C the equilibrium constant K_P of the reaction: $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is 2.9×10^{-2} atm. Calculate the degree of dissociation when the total equilibrium pressure is 1.00 atmosphere. [Ans. 0.17]

21. For the dissociation :

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

at 247 °C the equilibrium constant K_p is 1.06. Calculate (a) the standard free energy change of the reaction and (b) the degree of dissociation at this temperature. [Ans. (a) – 290.5 J; (b) $\alpha = 0.718$]

22. At 900 K the equilibrium constant K_p of the reaction :

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

is 6.55. (a) Calculate $\Delta G°$ value for the reaction at this temperature. (b) If K_p = 1.86 at 1000 K, what is the heat of the reaction, assuming that the value is constant over the temperature range.

[Ans. (a) –14.1 kJ; (b) –94.5 kJ]

11 PHASE EQUILIBRIA

In the previous chapter equilibria in heterogeneous systems, such as liquid - vapour, solid - liquid etc. have been discussed in terms of the kinetic theory and from the view point of thermodynamics. Since heterogeneous equilibria exist between two or more different phases, these are also known as *phase equilibria.* The conditions of equilibria between the various phases of a substance can be represented simultaneously on a single graph which is known as a *phase diagram*. Heterogeneous equilibria or phase equilibria may also be described in terms of a very important and exact generalization known as the *phase rule.* The rule is based purely on thermodynamics and is applicable to all macroscopic systems involving heterogeneous equilirbria. It is independent of atomic or molecular structure. When properly applied to systems at true equilibria, the rule gives clearly and unequivocally the maximum number of phases that can co-exist under a set of conditions and puts a limit to the variables of the systems such as temperature, pressure, concentration etc. It does not, however, consider the effect of gravitation, electrical and magnetic fields and surface forces. The rule also does not say anything about the time required for a certain reaction to be complete or the time required for the attainment of equilibrium. The phase rule, discovered by William Gibbs(1874), can be mathematically stated as follows :

$$F = C - P + 2$$

where F is the number of *degrees of freedom,* C is the number of *components* and P is the number of *phases.*

If a small quantity of a volatile liquid is introduced in the Torricellian vacuum, the liquid passes to the vapour phase and exerts a pressure causing a depression of mercury meniscus (*Section 3.1* and Figure 3.1). When sufficient liquid is introduced, a heterogeneous equilibrium between liquid and vapour is established and the liquid exerts a definite vapour pressure at a definite temperature. Two important conclusions can be drawn:

(i) The pressure exerted is a function of the quantity of the liquid up to a certain limiting quantity of the liquid and

(ii) The pressure is independent of the quantity of liquid after the limit has been exceeded and is called the *saturated vapour pressure* of the liquid. In the latter case only temperature influences the vapour pressure.

Thus in the unsaturated state vapour will obey the gas laws but in the saturated case involving heterogeneous system at equilibrium, the pressure will be governed by the Clausius-Clapeyron equation (*Section7.15*).

11.1 Definition of Terms

Before describing the phase rule and applying it to specific systems, three terms must be defined and explained. The meaning and significance of these terms, (i) *phase,* (ii) *component* and *(iii) degrees of freedom,* are to be thoroughly understood as a prerequisite to the study of phase rule.

(i) **Phase** (*P*): A phase may be defined as :

The homogeneous part of a heterogeneous system which is physically and chemically different from other parts of the same system and bounded by surfaces of separation and mechanically separable.

A system can consist of one or more phases. Some examples are given below:

One phase systems:

(a) *A pure substance in one physical state.*

(b) *A mixture of liquids which are completely miscible with each other in all proportions is one phase in the liquid state, e.g., H_2O/Alcohol etc.*

(c) *A pure gas or a mixture of gases which do not react with each other.*

(d) *A solution of a solid in a liquid, $NaCl/H_2O$, Sugar/H_2O etc.*

(e) *A mixture of solids in the molten state.*

Two phase systems:

(a) *A pair of immiscible liquids, e.g., CCl_4/H_2O, $C_2H_2Cl_2/H_2O$, etc.*

(b) *A liquid and its vapour.*

(c) *A solid substance and its liquid phase or vapour phase.*

(d) *A mixture of solids in the liquid (molten) phase and one of the solids in the solid phase.*

(e) *A mixture of two solids which do not react with each other.*

Three phase systems:

(a) *A pure substance existing in three phases together, e.g. ice, water and water vapour*

(b) *A solid in two allotropic forms and the liquid mixture or in vapour phase.*

(c) *A mixture of two solids in the molten form and the two solids.*

(ii) **Component** (*C*)**:** The number of component is defined as

The minimum number of independently variable chemical entities required to describe all parts of a system

These chemical entities may undergo chemical reaction or physical changes or both, with an increase or decrease of different entities; the number of phases may also change depending on the nature of the changes. To define the equilibrium conditions of the system it will not be necessary to consider all the chemical entities. There can be systems of one, two or more components. Few examples are given below :

One component systems:

(a) *Water:* Water may exist in three different phases, solid, liquid and vapour. In each case the chemical entity is H_2O.

(b) *Sulphur:* Sulphur can exist in four phases – two allotropes (a) monoclinic (s), and (b) rhombic (s), as a liquid and as vapour. Again in all these phases the chemical constituent is the same.

Two component systems:

(a) If $CaCO_3$ is heated in a closed container it undergoes dissociation forming CaO and CO_2. When the system attains equilibrium all three chemical substances are present. These three chemical entities are related by the equation

$$CaCO_3(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

There will be three phases, each of the chemical entities representing a phase as they are bounded by a separate boundary, but *the number of components will be* **two** because all the three phases can be described by mentioning any two of them as they are related by the above equation.

(b) A solution of $NaCl$ is a one phase system. The *number of components* in the system is, however, two as the concentration can vary and the composition of the system cannot be described by mentioning any one of them. Similarly *the number of components* in a saturated solution of the salt is also two for the same reason.

(c) Systems in which salts form one or more hydrates are two component systems as the composition of all phases (hydrates) and water can be described by the constituents, e.g. the salt and water.

(d) Pairs of partly miscible or immiscible liquids.

(e) Pairs of metals which are miscible in the liquid phase but form separate pure solid metal phases.

(iii) **Degrees of Freedom** (F)**:** The number of degrees of freedom (or variance) may be defined as,

> *The number of independent variables e.g, temperature, pressure and composition, which must be fixed in order to define the system completely.*

A system with $F = 2$ is called bivariant
A system with $F = 1$ is called univariant
A system with $F = 0$ is called invariant

Three examples are :

(a) *A gaseous system :* The temperature, pressure and volume of a gas are related by an equation of state, $PV = RT$. The state of the gaseous system is completely defined by any two of the three variables. The third is automatically fixed. This is a *bivariant* system, i.e., the degree of freedom is two.

The $t - c$ curve of a mixture showing a maximum is shown in Figure 11.17, the upper curve is for the vapour while the lower one is for the liquid as in previous cases, and a and b are the boiling points of the pure components. At the point c the mixture has a maximum boiling point and the liquid and vapour in equilibrium have the same composition. If a mixture of composition c is vaporized and then condensed the distillate will have the same composition as the original liquid. *A mixture which distils without change in composition is known as an azeotrope or an azeotropic mixture.* A common example of such systems is $H_2O - HCl$.

When a mixture forms an azeotrope, complete separation of the liquids by simple fractional distillation is not possible. Referring to Figure 11.17 if one starts with a mixture having composition corresponding to a point to the left of the azeotrope, the distillate will gradually be enriched in A but the liquid will become richer in B until the azeotropic composition is reached. If, on the other hand, one starts with the liquid mixture of composition corresponding to a point to the right of the azeotrope the liquid will get enriched in A until the azeotropic composition is reached. Liquid of this composition distils unchanged in composition.

The situation becomes similar if the t-c diagram has a minimum as shown in Figure 11.18. From whatever side of the azeotrope one may start distillation, the composition soon reaches the azeotropic value and the solution continues to boil at constant temperature like a pure liquid and prevents any further separation. Alcohol-water, *n*-propanol-water, acetone-carbon disulphide are a few examples of liquid pairs showing minimum in the t-c diagram.

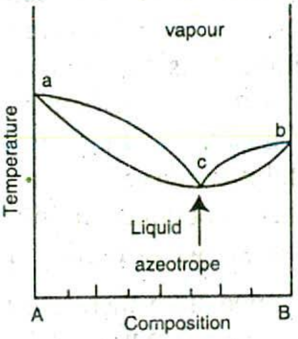


Figure 11.18 t-c diagram

The azeotropic mixtures boil at constant temperatures and distil over without any change of composition at a given pressure. If, however, the pressure is changed, both the boiling temperature as well as composition change. This is unlike pure compounds. For pure compounds the boiling temperature is changed with change of pressure, but not the composition. For example, H_2O boils at 100°C at atmospheric pressure, but on the top of a mountain the boiling temperature will be much lower because the pressure is lower. The composition, however, will always be H_2O. In other words, an azeotrope is a mixture, and not a compound.

11.12 Liquid–Liquid Equilibria in Partly Miscible Systems : Critical Solution Temperature (CST)

There are pairs of substances which are liquids at ordinary temperatures or whose melting points are low, or are known to have limited mutual solubility within certain temperature limits. They are said to be partly miscible in the temperature limits and their solubility curves form an interesting aspect of the application of the phase rule. These substances become completely miscible beyond the temperature limits. These limits are sometimes attained on raising the temperature or sometimes on lowering the temperature. In some systems there are two limits, one higher and the other lower. In this section an attempt will be made to discuss a few systems.

(i) *Phenol-water system:* If a small quantity of phenol is added to water at the ordinary temperature the phenol dissolves completely and a clear solution results. On further addition of phenol the dissolution goes on until around 7% of phenol is in solution when a turbid mixture, resembling an emulsion, is obtained. If the mixture is allowed to stand two liquid layers separate out – the upper layer is a solution of phenol in water and the lower layer a solution of water in phenol. If this mixture is slowly heated, at a certain temperature the two liquids again form a clear solution and complete miscibility results. Let this temperature be t_1, and the composition c_1. Let a little more phenol be added when the composition becomes c_2 and the turbidity again appears. The turbid mixture is again heated and at temperature t_2 the system again becomes completely miscible. In this way a complete solubility curve can be obtained. If all the points so obtained are plotted a *t-c* curve results as shown in Figure 11.19.

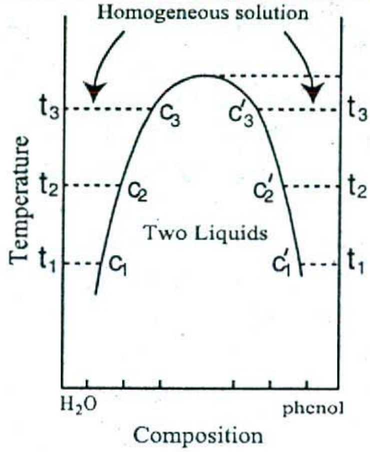


Figure 11.19 *t-c* diagram of phenol – water system

At each temperature there are two compositions, say c_1 and c'_1, one representing the composition of phenol in water (c_1, c_2 *etc.*) and the other in a solution of water in phenol (c'_1, c'_2 etc.). These solutions shown by c_1 and c'_1, c_2 and c'_2 etc. are called *conjugate solutions.* As the temperature is raised to t_2, t_3 etc. c_2 and c'_2, c_3 and c'_3 approach each other until at 66°C the two curves meet and complete miscibility results. At 66°C and upwards the two components are completely miscible in all proportions. This temperature is called the *critical solution temperature or consolute temperature (CST).* The limiting composition of the solution at the critical solution temperature is difficult to evaluate from the graph because the composition axis near the consolute temperature is somewhat flat. The computation is best done by joining the composition of conjugate (Figure 11.20) solutions c_1 and c'_1, c_2 and c'_2 etc. by horizontal lines c_1 c'_1, c_2 c'_2 etc. The horizontal lines are called *tie lines.*

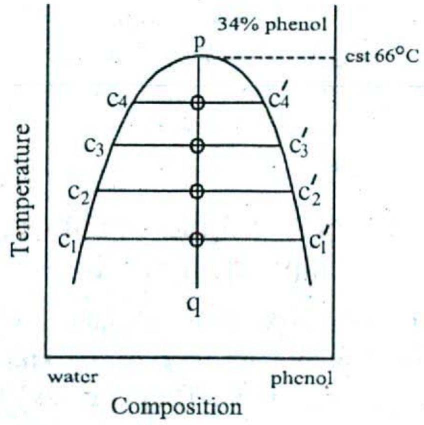


Figure 11.20 *t-c* diagram of water-phenol

The middle points of these tie lines fall on a straight line *pq* and this cuts the solubility curve at a point *p*, which gives the correct composition (Figure 11.20). These middle points of the tie lines are indeed the arithmetic means of composition c_1 and c'_1, c_2 and c'_2 etc. The line *pq* resembles the line joining the mean densities of liquid and vapour according to the *law of rectilinear diameter* (see Figure 2.13). At all points on the curve c_1 c_2 c_3 c'_3 c'_2 c'_1 and within the area bounded by the above curve, there are two phases present and the degree of freedom of the system is, therefore, one ($F = 2 - 2 + 1 = 1$). This means that at constant temperature the solubility of one liquid in the other is constant. If temperature is altered the composition must vary by itself to maintain the equilibrium. If the temperature exceeds the *CST*, one phase disappears and the system becomes again bivariant.

A similar behaviour is shown by the system methyl ethyl ketone and water as shown in Figure 11.21.

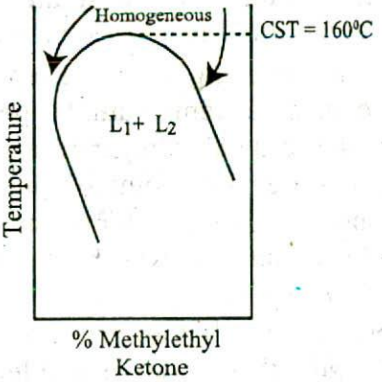


Figure 11.21 *t-c* diagram of water-methyl ethyl ketone

The critical solution temperature is very sensitive to the presence of a third component soluble in either of the two substances.

(ii) *Triethylamine-water:* This is a two component system where it is found that the mutual solubility decreases on raising the temperature and increases on lowering the temperature. The behaviour is just the reverse of phenol-water system. Solubility curve of water and triethylamine is shown schematically in Figure 11.22. At a temperature of 18°C and below the two components, water and triethylamine, are completely miscible in all proportions but above 18°C they are only partly miscible and two liquid layers L_1 and L_2 persist.

Critical solution temperature thus attained on lowering the temperature is known as the *lower consolute temperature* in order to differentiate it from *upper consolute temperature* as in the case of phenol-water. Thus mutual solubility of two partly miscible liquids may be increased by raising or lowering the temperature depending on the system. *Critical solution temperature or consolute temperature may, therefore, be defined as the temperature above or below which two partly miscible liquids become completely miscible in all proportions.*

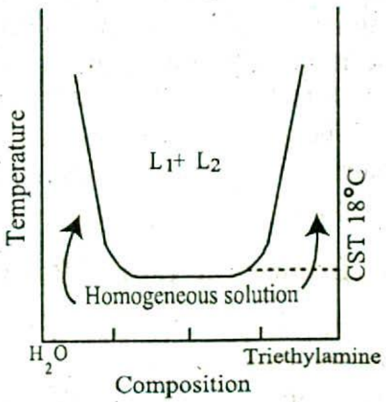


Figure 11.22 *t-c* diagram of water-triethytamine.

(iii) *Nicotine-water:* The system nicotine-water gives an interesting phase diagram which is a completely closed curve as can be seen in Figure 11.23. There are two critical solution temperatures one at 208°C and the other at 61°C. Within these temperature and concentration ranges shown in the figure partial miscibility persists and there are two liquid phases shown as L_1 and L_2. Outside these ranges complete miscibility results. This curve looks like the combination of Figures 11.20 and 11.22 which represent phenol-water and triethylamine-water respectively. Several other pairs are known to behave like nicotine-water.

In several cases the consolute temperature cannot be attained. This happens due to disappearance of one of the phases as vapour above the critical temperature or as solid below the freezing point. Theoretically their consolute temperatures lie either above the critical temperature or well below the freezing point of one of the components. Water-chloroform is an example of the first type because before the *CST* is attained the cirtical temperature of choloroform is reached. Water and ether is an example of the second type. Water freezes to ice before the lower consolute temperature can be attained.

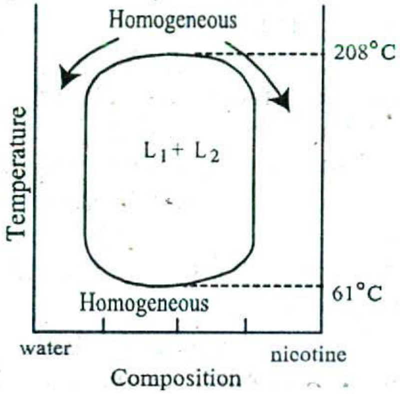


Figure 11.23 *t-c* diagram of water- nicotine

(iv) *Effect of pressure on critical solution temperature:* All systems so far described refer to constant pressure of the atmosphere or at any other constant pressure. Consequently, each *t-c* diagram is an *isobar*. However, if the pressure on such a system is changed the critical solution temperature is also found to change. The effect of pressure is governed by the Le Chatelier principle and the Clausius-Clapeyron equation. In general increase of pressure raises the lower *CST* and lowers the upper *CST*. Under appropriate pressures two *CST's* may coincide with each other giving rise to complete miscibility at all temperatures. At one atmosphere pressure the two critical solution temperatures for water and secondary butyl alcohol are −12 °C and 114°C but at about 840 atmospheres the two *CST's* are identical. However, it should be mentioned that although the lower *CST* is always raised by increase of pressure the upper *CST* may be lowered or raised by increase of pressure. The latter behaviour is not very common.

11.13 Immiscible Liquid Pairs: Steam Distillation

There are pairs of liquids which are insoluble in each other. When mixed in any proportion they separate into two layers. Such liquids are said to be immiscible with each other. Examples are: carbon tetrachloride/water, mercury/water, nitrobenzene/water, aniline/water.

If a pair of immiscible liquids is stirred, the vapour pressure above the mixture is found to be equal to the sum of the vapour pressure of the components *A* and *B*. Thus

$$p_{total} = p_A^0 + p_B^0$$

The total vapour pressure of the mixture is thus higher than the vapour pressure of any of the two components. A consequence of this is that the mixture boils at a lower temperature than any of the two components. This is shown in Figure 11.24. Here the vapour pressure of the two components *A* and water and that of the mixture at different temperatures are plotted. The vapour pressure of all three liquids increase with increasing temperature. When the total vapour pressure equals 1.0 atm the liquid will boil.

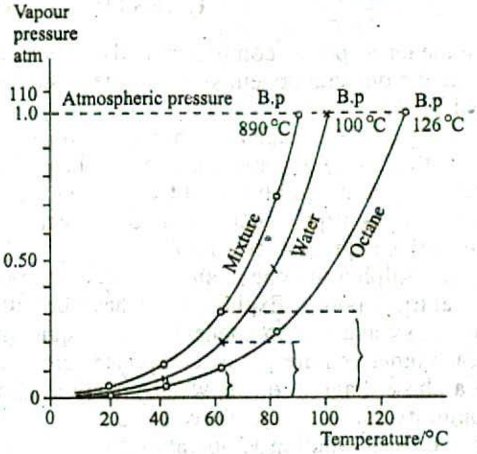


Figure 11.24 Change of vapour pressures of water obtained and a mixture of the two with temperature

As can be seen the mixture boils at a lower temperature than any of the pure liquids. This property of such mixtures has been used to separate/purify many organic liquids which are immiscible with water. The method is known as steam distillation.

A diagram of an apparatus used for steam distillation is shown in Figure 11.25. It consists of a round–bottomed flask F, having a glass inlet tube which reaches almost to the bottom of the flask and is connected to a steam generator G. The flask has also a glass outlet tube connected to a Liebig condenser.

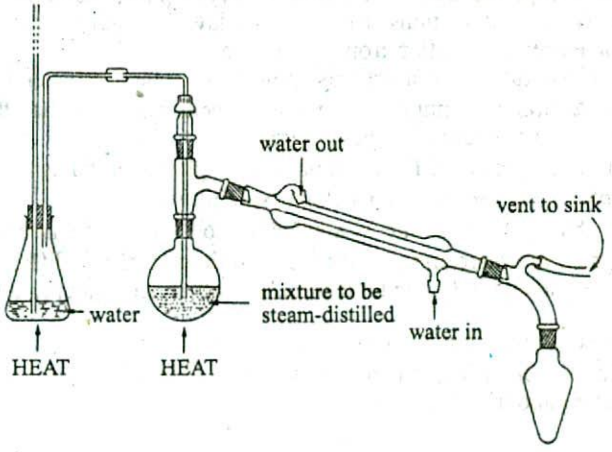


Figure 11.25 Apparatus for steam distillation.

The material to be steam-distilled is placed in F and a vigorous current of steam blown in from G. The mixture is thus rapidly heated, and the vapour of the organic compound mixed with steam passes over and condensed in E. The organic compound can be separated from water with the help of a separating funnel and dried by suitable means.

QUESTIONS AND PROBLEMS

1. Define the terms phase, component and degrees of freedom.
2. Describe the one component system water with the help of the phase diagram. Show the various zones in the diagram.
3. What is triple point? Explain with the help of a phase diagram.
4. Describe the system sulphur and draw a phase diagram. Show the triple points and explain clearly the different phases at equilibrium at these points.
5. Show that at the triple points and at the eutectic points the gree or freedom is zero. Is It possible to have negative degrees of freedom?
6. Water and sulphur are one component system, but water has only one triple point whereas sulphur has three real triple points. Explain this behaviour with the help of phase diagrams.
7. Describe a simple two component solid – liquid system where the components are completely miscible with each other and there is no compound formation.
8. Draw a phase diagram of the water-phenol system and explain the diagram clearly. What happens to the solubility curves at and above 66°C?
9. What is critical solution temperature? Explain with the help of a suitable phase diagram. What is a lower critical solution temperature?
10. In general what is the effect of pressure on the *CST* for systems which show closed solubility diagrams?
11. Deduce the phase rule $F = C - P + 2$. What is a condensed system? Write down the phase rule for a condensed system.
12. What is sublimation and how do you explain it from your knowledge of phase rule? Is sublimation a specific property of some substances? Justify your answer.
13. Describe a simple fractionating column. How does a fractionating column function?
14. Describe with suitable phase diagrams the conditions which govern the separation of two completely miscible liquids by fractional distillation.
15. Is it possible to separate completely two liquids in solution by fractional distillations? If not, state the reasons for the failure. Explain your answer with suitable phase diagrams.
16. What is an azeotropic mixture? Explain with a *t-c* diagram.
17. Show how the existence of compounds formed between two components, A and B, can be proved and the composition of the compound ascertained from a study of phase diagram.
18. Discuss the different types of deviations from Raoult's law for liquid pairs. What happens to the t-c diagrams if there is an extreme deviation from Raoult's law?
19. State and explain the phase rule and illustrate its application to the ice-water-vapour system.
20. What is triple point? Although sulphur is a one component system, it has three stable triple points. Explain this behaviour with the help of a phase diagram.
21. What is critical solution temperature? Describe briefly the phenol-water system. Name a partly miscible liquid pair showing a closed solubility curve.
22. State and explain the phase rule. Illustrate its application to the case of a freezing mixture.
23. Draw the phase diagram of water and discuss the significance of the different parts of the diagram. Show that there can he one and only one temperature at which ice, water and water vapour exist at the same time.
24. Discuss the principle of fractional distillation.
25. State the phase rule and explain fully the terms involved. Discuss the application of phase rule to the system ice-water- water vapour.
26. Write notes on :-
    (a) Triple point; (b) Eutectic mixture; (c) Azeotropic mixture (d) Fractional distillation; (e) Phase rule.
27. When various mixtures of A and B are cooled the following freezing points were found:

Mole %A	100	90	80	70	65	55	50	40	35	25	20	10	0
F. P. (°C)	98	95	90	85	82	82	83	80	75	70	77	83	87

Plot these data graphically, complete the phase diagram and name the different areas. What information do you obtain about the system A -B from the phase diagram?

12 KINETICS OF CHEMICAL CHANGE

Chemical reactions and physical processes require varying times for completion. Some are completed in a very short time, while others take a long time. For example, if you add sodium carbonate solution to a solution of calcium chloride an immediate white precipitate is seen, whereas the conversion of vegetable and animal remains to petroleum oil takes millions of years. Kinetics of chemical change, as the name suggests, deals with the rate at which a change proceeds along a certain direction. Thus chemical kinetics deals with the rate of disappearance of a reactant or rate of appearance of product in a chemical change. While other branches of physical chemistry do not say *'how fast'* or *'how slow'* is a reaction, chemical kinetics give a clear picture of *'fastness'* or *'slowness'* of a process

The study of the rates of reaction is of both theoretical and industrial importance. In industry, for example in the manufacture of ammonia, it is desirable to know how fast and under what conditions maximum or optimum (most desirable) yield of the product of the industry can be obtained. The study of rates of reaction allows scientists to understand the *mechanism* or *the sequence of steps* by which a reaction occurs.

12.1 The Definition of Rate of a Reaction

The rate of a reaction (rate) is the amount of reactant used up or the amount of product formed in unit time. In application in chemistry the amount is expressed in moles, or more usually in mol L^{-1}. The rate of a chemical reaction is the decrease of concentration (in mol L^{-1}) of the reactant or increase in the concentration of the product in unit time. The unit of the rate is usually expressed as mol L^{-1} s^{-1} (or min^{-1}, h^{-1} etc. depending on the *'fastness'* or *'slowness'* of the reaction).

Let us consider the hypothetical reaction

$$A \rightarrow B \tag{12.1}$$

As the reaction proceeds the concentration of A decreases and that of B increases. If the increase and decrease are simply stated as the change in concentration then

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} \tag{12.2}$$

Or

$$= +\frac{\Delta[B]}{\Delta t} \tag{12.3}$$

Note the different signs in the two expressions. In the equation (12.2) the negative sign indicates that the concentration of the reactant A decreases with the progress of reaction, and the positive sign in equation (12.3) signifies that the concentration of the product B increases with time.

Example 12.1 **:** In the study of the reaction mentioned above the concentration of the reactant A is 0.20 mol L^{-1} at time 15 seconds after the start of the reaction and the concentration is 0.12 mol L^{-1} after 75 seconds from the start. Calculate the rate of the reaction.

Solution: Here $\Delta[A]$ is (0.20 – 0.12 =) 0.08 mol $L^{-1}$and Δt is (75 – 15 =) 60 seconds. Hence the rate is,

$$\frac{\Delta[A]}{\Delta t} = \frac{0.08 \text{ mol L}^{-1}}{60 \text{ seconds}}$$

$$= 1.33 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

This, however, is the average rate between the period from 15 seconds to 75 seconds after the start of the reaction.

More important and useful is the determination of the rate at a particular time after the start of the reaction. Suppose one wants to find the rate 50 seconds after the start of the reaction. Obviously the above data will not give the information. A graphical method is to be used for the purpose.

If the concentration of A is determined at different times after the start of the reaction the data can be represented in the form of a graph as shown in Figure 12.1. Similarly if the concentration of the product B is determined at different times after the start of the reaction the data will be represented by a graph as shown in Figure 12.2.

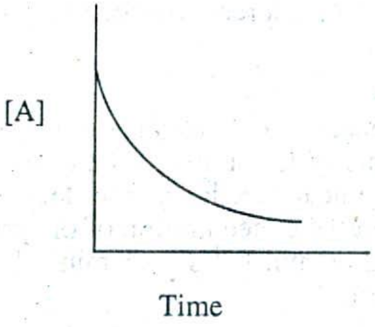


Figure 12.1 Concentration of A *vs* time

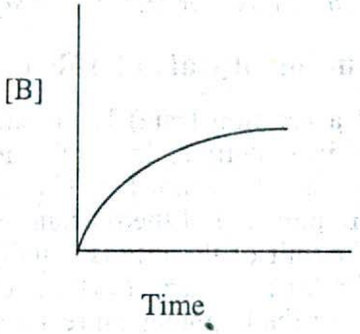


Figure 12.2 Concentration of B vs time

The rate of the reaction at any time can be determined by drawing a tangent to the curve at that particular time and finding the gradient (slope) of the curve as shown in Figure 12.3. The slope of the tangent is the rate of the reaction at that particular time. The slopes of the tangents drawn at different times on the curve become smaller with increase of time indicating that the rate decreases as the reaction proceeds. These rates are what are called *instantaneous rates*, that is, the rates at particular instants.

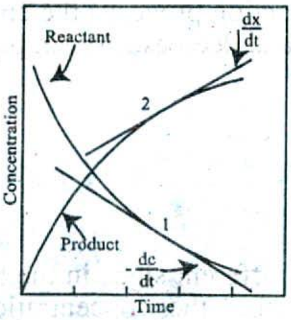


Figure 12.3 Concentration of reactant and product *vs* time

When we measure the change of concentration ΔA over a period of time Δt the rate as written is the average rate over the period of time. This must be because the rate is changing every instant as the nature of the curves (Figure 12.1 and 12.2) show.

For a reaction such as, $A + 2B = 3C + D$, one can write the rates as

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t} = \frac{1}{3}\frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t} \tag{12.4}$$

Since the concentrations of the products are increasing the last two terms are positive. One should note that the rate of decrease of concentration of A is equal to half the rate of decrease of concentration of B as when one mole of A reacts two moles of B react.

12.2 Experimental Determination of the Rate of a Reaction

Various experimental procedures have been used to determine the rates of reactions. For different reactions different methods may have to be used. As we have seen, for the determination of the rate of a reaction one has to determine the concentration of the reactant or the product at different intervals of time. A few examples are mentioned.

(a) Hydrogen peroxide decomposes in the presence of manganese (IV) oxide according to the equation below:

$$2H_2O_2(l) \rightarrow H_2O(l) + O_2(g)$$

A gas is evolved as a result of the reaction. So the rate may be found by measuring the volume of gas evolved at different times.

(b) If a reaction is slow then a fixed volume of sample of the reaction mixture can be withdrawn at intervals and the concentration determined by chemical analysis. As the reaction continues to proceed, in the sample taken it is the practice to '*freeze*' the reaction before analysis. Freezing means to substantially reduce the rate of the reaction. This can be done (i) by rapidly cooling the sample to a low temperature, (ii) by adding a chemical which will remove one of the reactants without affecting the others or (iii) by dilution to a large volume. An example is the hydrolysis of ethyl acetate by aqueous sodium hydroxide solution.

$$CH_3COOC_2H_5(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + C_2H_5OH(aq)$$

The reaction can be followed by titration of the samples with standard hydrochloric acid solution as the concentration of $NaOH$ gradually decreases as the reaction proceeds

(c) A less cumbersome method is to follow the change of some physical property as the reaction proceeds. For example the above reaction can be followed by measuring the conductivity of the solution at different times. Samples do not have to be removed for the purpose. As the reaction proceeds the concentration of $NaOH$ decreases and so also the conductivity since the conductivity of sodium acetate is less than that of sodium hydroxide. The change in conductivity can be related to change in concentration (*Section 12.6.3*).

A second example of this type is the study of the rate of inversion of sucrose into glucose and fructose in the presence of an acid by using a polarimeter which is used to measure the angle of rotation of the plane of polarization of plane polarized light (*Section 12.6.3*).

Another method which is widely used is the measurement of the intensity of radiation with time in cases where absorption of radiation in the visible or *UV* region of the electromagnetic spectrum changes as the concentration of a reactant or product changes as the reaction proceeds. Consider the reaction

$$ClO^-(aq) + I^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$$

The ion $IO^-(aq)$ absorbs radiation of wavelength in the neighbourhood of 400 nm. The absorption of this radiation is proportional to the concentration of IO^- ion, and one can use the spectrophotometer to determine the rate of the reaction by finding the relation between the concentration and intensity of radiation absorbed.

Any physical property of a substance which changes with concentration can be used provided the method of measurement is suitable.

12.3 Factors Affecting the Rates of Reaction

Experiments show that the rates of reactions are affected by several factors or variables. These are:

(a) Concentration of the reactant
(b) Pressure (in the case of gases)
(c) Temperature of reaction
(d) Catalyst
(e) Surface area of solid reactant or catalyst

And, in some cases, light.

The effect of concentration, pressure and surface area on the rate of a reaction can be simply explained if one recognizes that in order for a reaction to take place reactant particles must collide with each other. More the number of collisions in unit volume in unit time higher is the rate of a reaction. The effect of temperature is two-fold:

(i) increase of temperature increases the kinetic energy of the reactant species bringing about an increase in the frequency of collisions,
(ii) at higher temperature more reactant species have the required energy of activation (*Section 12.9*).

Both of these factors increase the rate when temperature is increased. A catalyst provides an alternative path with lower activation energy for the reaction so that in the presence of a catalyst more reactant species have the necessary activation energy and the rate increases. Well known examples of the effect of light on the rate of a reaction are photosynthesis and the reaction of hydrogen and chlorine, which do not take place in the absence of light.

12.4 Dependence of Rate on Concentration: The Rate Law

Experiments show that the rate of a reaction depends on the concentration of one or more of the reactants (and also of catalysts). We will consider the effect of the catalysts in Chapter 13.

For a reaction in which the rate is dependent on the concentration of the reactant A the experimental results can be expressed as

$$\text{rate} \propto c^n \tag{12.5}$$

This can be expressed as

$$\text{rate} = k\,c^n \tag{12.6}$$

where k is a constant of proportionality and is called the *rate constant* (or *the specific reaction rate* when unit concentration is considered), c is the concentration of A and n is a constant for that reaction and is called the *order of the reaction*. The rate constant varies with temperature but is independent of concentration. Equation (12.6) is known as *the rate law* or *the rate equation* for the reaction. *The rate constant k is defined as the proportionality constant between the rate and the concentration term (concentration with its power).* One can also see that rate constant k is equal to the rate when the concentration is one mol L^{-1}. The order of the reaction tells us the exact relation between the rate and the concentration. *The order of a reaction can be defined as the power to which the concentration is to be raised in order to make the concentration term (concentration with its power) proportional to the rate.*

In general for a reaction, $A + B \rightarrow$ *product/products,* in which the rate is dependent on the concentrations of the reactants A and B we can write

$$\text{rate} = k\,c_A^m\,c_B^n \tag{12.7}$$

where

m	is called the order with respect to A
n	is called the order with respect to B
$m + n$	is called the overall order of the reaction
c_A	is the concentration of A
c_B	is the concentration of B

The type of dependence, ***which is always determined by experiment***, is peculiar to a particular reaction. Some examples are:

(a) In the reaction $2\,N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

the rate is directly proportional to the concentration of $N_2O_5(g)$. So the rate equation for this reaction is

$$\text{rate} = k\,[N_2O_5] \tag{12.8}$$

In this expression the value of n is one. So it is called a *first order* reaction.

(b) In the reaction $C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$

the rate is proportional to the concentration of C_2H_5Br and of OH^-. So the rate equation is

$$\text{rate} = k\,[C_2H_5Br]\,[OH^-] \qquad (12.9)$$

In this reaction the order with respect to C_2H_5Br is one and the order with respect to OH^- is also one. The overall order is (1 + 1 = 2) two.

(c) In the reaction $(CH_3)_3CBr(aq) + OH^-(aq) \rightarrow (CH_3)_3COH(aq) + Br^-(aq)$ the rate is directly proportional only to the concentration of $(CH_3)_3CBr$. So the rate equation is

$$\text{rate} = k\,[(CH_3)_3CBr] \qquad (12.10)$$

and the order of the reaction is one. Since the rate does not depend on concentration of OH^- the order with respect to OH^- ion is said to be zero.

(d) In the reaction $2NO(g) + 2H_2(g) = N_2(g) + 2H_2O(g)$ the rate is proportional to the concentration of $H_2(g)$ and to the square of the concentration of $NO(g)$. The rate equation for this reaction is

$$\text{rate} = k\,[NO]^2[H_2] \qquad (12.11)$$

In this reaction order with respect to NO is two and order with respect to H_2 is one and the overall order is (1+2 = 3) three.

There are some reactions where the rate is not dependent on the concentration of a reactant as in (c) above in which the rate is independent of the concentration of OH^-. Such reactions are known as zero order reaction. One also finds reactions of fractional order like ½, ⅓ etc.

It is clear from the above examples that the order of a reaction is an experimental quantity and does not depend on the co-efficients of the reactants in the balanced chemical equation for the reaction.

12.5 Units of Rate Constants

The units of rate constants are derived from the rate equation and depend on the order of the reaction. Thus considering time in second the units of k are given in the Table 12.1 below:

Table 12.1 Units of the rate constants

Order of reaction	Unit of k
Zero	$mol\ L^{-1}\ s^{-1}$
First	s^{-1}
Second	$L\ mol^{-1}\ s^{-1}$
Third	$L^2\ mol^{-2}\ s^{-1}$

12.6 Determination of the Rate Law: Determination of Order of Reactions

From the rate equations (12.6) to (12.11) it can be seen that to establish the rate law of a reaction it is necessary to find the order of the reaction with respect to each of the reactants. For this purpose several methods are available. For a particular reaction a suitable method can be used.

12.6.1 Initial rate method

The method consists in carrying out several experiments for the same reaction in which the starting or initial concentration of the reactant is different. In each experiment the concentrations of the reactant at different times are determined and the data are plotted as concentration versus time as shown below in Figure 12.4.

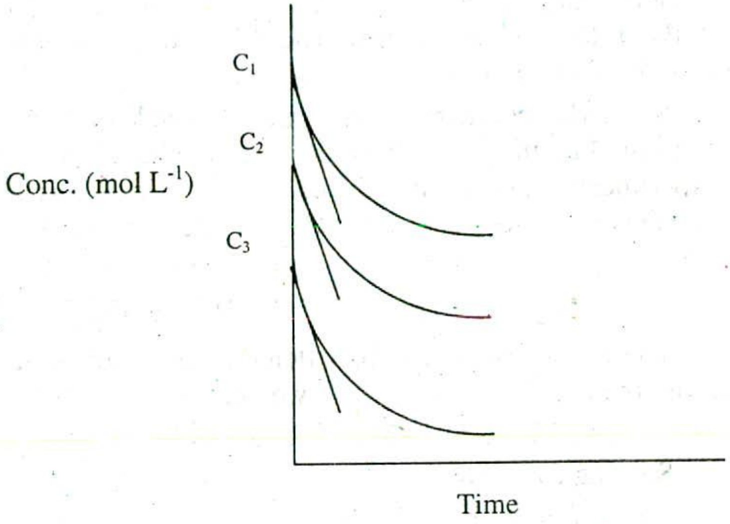


Figure 12.4 Concentration *vs* time

A tangent to the curve at the initial concentration is drawn and the gradient of the tangent gives the initial rate. The initial rates for different concentrations are compared from which the order of the reaction can be determined.

In cases where the rate depends on the concentrations of more than one reactant, for example *A* and *B*, two or more experiments are done in which the concentration of one of the reactants, say *A*, is kept constant while the initial concentration of *B* is different. Again two or more experiments are done in which the concentration of *B* is kept constant while the initial concentration of *A* is different. The subsequent procedures are the same as in the first example. An illustration of such cases is given below.

Example 12.2: In a series of experiments between nitric oxide and bromine

$$2NO\,(g) + Br_2\,(g) \rightarrow 2NOBr_2\,(g)$$

carried out at 273°C the following data were obtained:

	Initial concentration (mol L^{-1})		Initial rate (mol L^{-1} s^{-1})
Experiment	*[NO]*	*[Br_2]*	
1	0.10	0.10	12
2	0.10	0.20	24
3	0.10	0.30	36
4	0.20	0.10	48
5	0.30	0.10	108

Determine the rate law for the reaction and calculate the rate constant.

Solution: Since there are two reactants we can tentatively write the rate equation as follows :

$$\text{rate} = k\,[NO]^m\,[Br_2]^n$$

In experiments 1 to 3 the concentration of *NO* is kept constant and concentration of Br_2 is varied. When the concentration of Br_2 is doubled (experiments 1 and 2) the rate becomes double; when the concentration of Br_2 is made three times (experiments 1 and 3) the rate also becomes three times. This can only be explained if the rate is directly proportional to the concentration of Br_2 or *the order with respect to* Br_2 *is one.*

Similarly, comparing experiments 1 and 4, when the concentration of Br_2 is kept constant but that of *NO* is doubled the rate becomes four times. Again comparing experiments 1 and 5 when the concentration of Br_2 is kept constant and the concentration of *NO* is increased by a factor of 3 the rate increases 9 times. These lead to the conclusion that *the order with respect to NO is 2.* Therefore,

$$\text{rate} = k\,[NO]^2\,[Br_2]$$

The rate constant can be calculated using the data for any one of the experiments. From the data for experiment 1 we get,

$$12 \text{ mol L}^{-1}\text{ s}^{-1} = k\,(0.10 \text{ mol L}^{-1})^2\,(0.10 \text{ mol L}^{-1})$$

Solving for *k*, we have,

$$k = (12 \text{ mol L}^{-1}\text{ s}^{-1}) / (0.10 \text{ mol L}^{-1})^2\,(0.10 \text{ mol L}^{-1})$$
$$= 1.2 \times 10^3 \text{ L}^2\text{ mol}^{-2}\text{ s}^{-1}$$

Example 12.3: In experiments of the reaction of tertiary–butyl bromide, $(CH_3)_3CBr$ with hydroxide ion, OH^-, at 55°C

$$(CH_3)_3CBr(aq) + OH^-(aq) = (CH_3)_3COH(aq) + Br^-(aq)$$

the following data were obtained :

	Initial concentration (mol L^{-1})		Initial rate of formation of (mol L^{-1} s^{-1})
Experiment	$[(CH_3)_3CBr]$	$[OH^-]$	$(CH_3)_3COH$
1	0.10	0.10	0.0010
2	0.20	0.10	0.0020
3	0.30	0.10	0.0030
4	0.10	0.20	0.0010
5	0.10	0.30	0.0010

Calculate the rate law and the value of the rate constant at this temperature.

Solution: As there are two reactants we can write the rate equation tentatively as below :

$$\text{rate} = k\,[(CH_3)_3CBr]^m\,[OH^-]^n$$

Using the same approach as in the previous example we can find the values of *m*, *n*, and *k*.

In experiments 1, 2 and 3 the initial concentration of OH^- ion is kept constant. Comparing experiments 1 and 2 when the concentration of $(CH_3)_3CBr$ is doubled the rate is also double. Again considering experiments 1 and 3 when the concentration of $(CH_3)_3\ CBr$ is increased by a factor of 3 the rate becomes three times. Order with respect to $(CH_3)_3CBr$ is 1, i.e., the value of m is 1.

In experiments 1, 4 and 5 the concentration of $(CH_3)_3CBr$ is kept constant while that of OH^- ion is varied. In each case the value of the rate remains unchanged. The conclusion is that the rate of the reaction is independent of the concentration of OH^- ion. Or in other words *the reaction is zero order with respect to* OH^- *ion concentration* and the value of n is zero.

Hence the rate law for the reaction is

$$\begin{aligned}\text{Rate} &= k\,[(CH_3)_3CBr][OH^-]^o\\ &= k\,[(CH_3)_3CBr]\,.\,1\\ &= k\,[(CH_3)_3CBr]\end{aligned}$$

The value of k may be obtained by using the data for any of the above experiments. Using data of experiment 1

$$0.0010\ \text{mol L}^{-1}\ \text{s}^{-1} = k\ (0.10\ \text{mol L}^{-1})$$

$$k = (0.0010\ \text{mol L}^{-1}\text{s}^{-1}) / (0.10\ \text{mol L}^{-1})$$

$$= 0.010\ \text{s}^{-1}$$

The method can be generalized as follows. Suppose for the reaction

$$A + B + C \longrightarrow \textit{Products}$$

the rate law is,

$$\text{rate} = k\,[A]^l\,[B]^m\,[C]^n$$

where l, m, and n are the orders with respect to A, B and C respectively. To determine the values of l, m and n two experiments are done keeping the concentrations of B and C constant but with different initial concentrations of A, two experiments are done keeping the concentrations of A and C constant but with different initial concentrations of B, and two other experiments are done keeping the concentrations of A and B constant but with different concentrations of C. The data can be used as follows for finding value of l.

$$\frac{(\text{rate})_1}{(\text{rate})_2} = \frac{(k\,[A]_1^{\,l}\,[B]^m\,[C]^n)}{(k\,[A]_2^{\,l}\,[B]^m\,[C]^n)} = \left\{\frac{[A]_1}{[A]_2}\right\}^l$$

Since all quantities except l are known l can be calculated.

By writing similar equations the expressions for m and n can be derived and their values determined from experimental data.

12.6.2 Method based on integrated rate equations

For workable formulas the integrated forms of the rate equations must be derived.

(a) Zero order reaction

In a zero order reaction the rate is independent of the concentration of the reactants. For example, if the reaction

$$A \rightarrow B$$

is zero order then the differential form of the rate equation is

$$-\frac{dc_A}{dt} = k_0\, c_A^0 \tag{12.12}$$

($\frac{dc_A}{dt}$ gives the rate of change of concentration c_A of A with time (t) and the negative sign is used to indicate that the concentration of A decreases. Hence $-\frac{dc}{dt}$ is the rate)

Henceforth, for convenience we will use c instead of brackets '[ ]' for concentration.

Since $c_A^0 = 1$, the above equation becomes

$$-\frac{dc_A}{dt} = k_0 \tag{12.13}$$

This shows that for a zero order reaction the rate is equal to the rate constant and is independent of the concentration. Rearranging equation (12.13) and integrating without limits we get,

$$c_A = -k_0\, t + C \tag{12.14}$$

where C is a constant of integration. Equation (12.14) shows that a plot of concentration versus time should give a straight line as shown in Figure 12.5. A straight line indicates that the gradient is constant, i.e. the rate is constant. The slope of the line is $-k$.

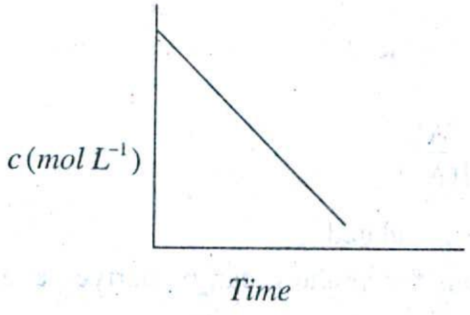


Figure 12.5 c *vs* time for zero order reaction

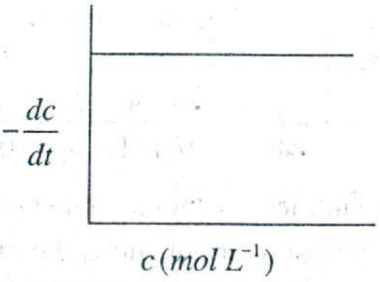


Figure 12.6 Rate *vs* c for zero order reaction

If, however, we plot rate versus concentration (equation 12.12) Figure 12.6 will be obtained.

Common examples of zero order reactions are photochemical reactions in which the amount of light is a controlling factor, and certain catalysed reactions in which the amount of catalyst determines the rate.

(b) *First- order reaction*

For a first order process in equation (12.6), $n = 1$ and hence

$$-\frac{dc}{dt} = kc \tag{12.15}$$

or

$$-\frac{dc}{c} = k\,dt \tag{12.16}$$

Integrating equation (12.16) between limits, concentration c_1 at time t_1 and c_2 at time t_2 ($t_2 > t_1$), we get,

$$-\int_{c_1}^{c_2} \frac{dc}{c} = k\int_{t_1}^{t_2} dt \tag{12.17}$$

or

$$-\ln c_2 + \ln c_1 = k(t_2 - t_1) \tag{12.18}$$

or

$$k = \frac{1}{(t_2 - t_1)} \ln\frac{c_1}{c_2} = \frac{2\cdot303}{(t_2 - t_1)} \log\frac{c_1}{c_2} \tag{12.19}$$

This form of the equation has the unique advantage that the initial concentration c_o at t = 0 (i.e., at the start of the reaction) need not be known. As a matter of fact, in many reactions c_o cannot be ascertained with any degree of accuracy. In such cases the above equation can be used to calculate the value of k. However, if c_o is known we get another expression,

$$k = \frac{1}{t} \ln\frac{c_0}{c_t} = \frac{2.303}{t} \log\frac{c_0}{c_t} \tag{12.20}$$

where c_t is the concentration at time t. Equation (12.20) can be rearranged to

$$k\,t = 2.303\,(\log c_0 - \log c_t)$$

or

$$\log c_t = -\frac{kt}{2.303} + \log c_0 \tag{12.21}$$

As one can see, this (equation 12.21) is an equation of a straight line of the form

$$y = m\,x + C$$

($y = \log c_t$, $m = -k/2.303$, $x = t$ and constant $C = \log c_0$)

A graphical representation of the values of $\log c_t$ at various t (equation 12.21) would be as shown in Figure 12.7. Alternatively, a plot of $\log \frac{c_0}{c_t}$ vs t (equation 12.20) gives a straight line with slope k as shown in Figure 12.8.

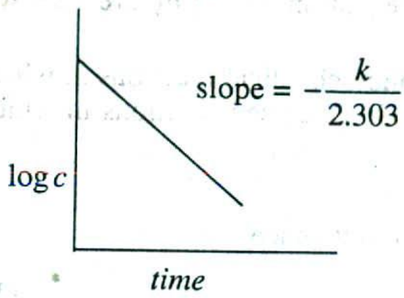


Figure 12.7 log c_t vs t for 1st-order reaction

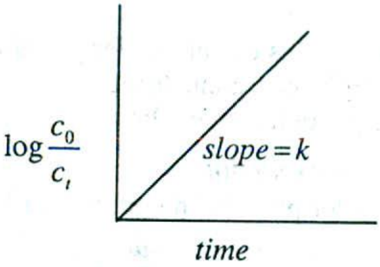


Figure 12.8 log $\frac{c_0}{c_t}$ *vs t* for first-order reaction

An alternative form of first-order rate equation

If a is the initial amount of reactant in a given volume and x be the amount reacted at any time t, then $a - x$ is the amount remaining unreacted and equation (12.20) assumes the form

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \tag{12.22}$$

or

$$k\,t = 2.303 \log \frac{a}{a-x} \tag{12.22a}$$

or

$$\log (a-x) = \log a - \frac{kt}{2.303} \tag{12.23}$$

A plot of $\log \frac{a}{a-x}$ vs time (equation 12.22a) would give a straight line passing through the origin (Figure 12.9). The slope of the line gives the rate constant k.

Alternatively, a plot of $\log (a-x)$ vs time according to equation (12.23) would also give a straight line (Figure 12.10), but with a slope of $-k$.

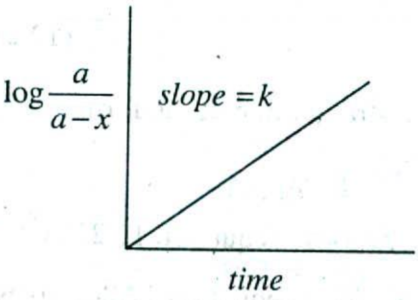


Figure 12.9 log $\frac{a}{a-x}$ vs *time*

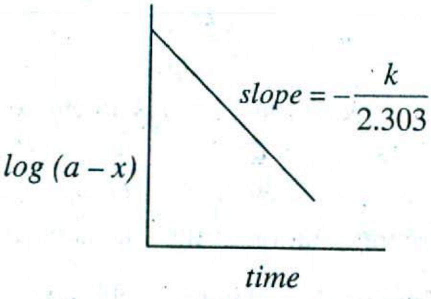


Figure 12.10 *log (a – x)* vs *time*

Other useful forms of first-order reaction equation

Equation (12.20) can be reorganized as,

$$\ln\frac{c_0}{c_t} = kt \text{, or} \quad \ln\frac{c_t}{c_0} = -kt$$

or,
$$c_t = c_0\, e^{-kt} \qquad (12.24)$$

Similarly from equation (12.23) we can write,

$$(a-x) = a\,e^{-kt}$$

or
$$x = a(1-e^{-kt}) \qquad (12.25)$$

Equations (12.24) and (12.25) show that the concentrations of the reactants fall off exponentially. However, in whatever form a first order rate equation may be written, *k* will have the dimension of reciprocal of time, i.e., sec^{-1}, min^{-1} or $hour^{-1}$, depending on the unit of time used, but *k* is independent of the unit of concentration.

Half – Life of a First-order Reaction

As a reaction proceeds the concentration of the reactants decreases, as these are used up. The half-life, $t_{1/2}$, of a reaction *is the time taken for the concentration of the reactant to decrease to half its initial value.*

The integrated rate equation (12.20) or (12.22) may be used to find an expression for the half-life of a reaction.

$$\text{At time } t_{1/2}, \qquad c = (1/2)\,c_0$$

Substituting this value in equation (12.20)

$$k\,t_{1/2} = 2.303\,\log\frac{c_0}{(1/2)c_0} = 2.303\,\log 2$$

or
$$t_{1/2} = \frac{2.303\log 2}{k} = \frac{0.693}{k} \qquad (12.26)$$

Substituting $x = (1/2)a$ at $t_{1/2}$ in equation (12.22) one obtains the same relation as in equation (12.26).

We can see that for a first order reaction the half-life is constant and independent of concentration. This is a very important characteristic of a first order reaction.

It is evident that a first order reaction is never complete. Let us suppose that the $t_{1/2}$ for a reaction is 5 minutes, i.e., after 5 minutes from the start half of the reactant has undergone reaction leaving one – half unreacted. In the next 5 minutes ½ of the remaining ½ would react; in the next 5 minutes ½ of the unreacted part will react and so on. This implies that such a reaction will be complete only after infinite time.

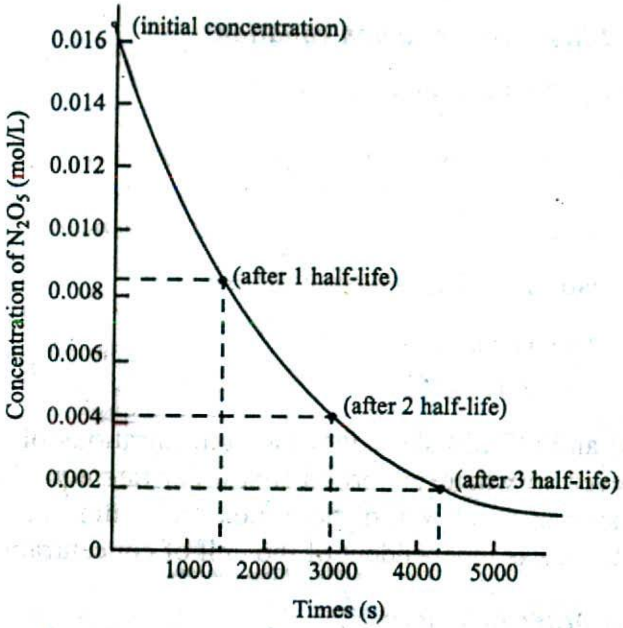


Figure 12.11 A graphical illustration to show how the half-life of a first-order reaction is independent of initial concentration.

Example 12.4: The decomposition of N_2O_5 dissolved in CCl_4 is a first-order reaction.

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

At 45°C starting with a solution of concentration 1.00 mol L^{-1} after 3.00 hours the concentration decreased to 1.21×10^{-3} mol L^{-1}. Calculate the half-life in minutes of the decomposition of N_2O_5 at 45°C.

Solution: To obtain the half-life the value of k must be found out. Since the reaction is first-order we can use equation (12.20).

$$k = \frac{2.303}{3\times60} \log \frac{1.00}{1.21\times10^{-3}}$$

$$= 0.0374$$

Now using Equation (12.26), $t_{½} = \frac{0.693}{k} = \frac{0.693}{0.0374}$

$$= 18.5 \text{ minutes}$$

Calculation of time for a definite fraction of a reaction

As for the calculation of half-life it may be shown that the time required for any definite fraction of a first order reaction to occur will be independent of the initial concentration. Let us calculate the time required for one third amount of the reactant to disappear. By using equation (12.22)

$$k=\frac{2.303}{t_{1/3}}\times log\frac{a}{\left(a-\frac{a}{3}\right)} \qquad \text{since } x=\frac{a}{3} \tag{12.27}$$

$$=\frac{2.303}{t_{1/3}}\times\left(log\frac{3}{2}\right)$$

Hence, $$t_{1/3}=\frac{2.303 log(3/2)}{k} \tag{12.28}$$

Example 12.5: For the reaction given in Example 12.4, calculate the time required to complete (a) 1/3rd of the reaction, (b) 80% of the reaction.

Solution: (a) Using equation (12.28) and the value of k obtained in Example 12.4 we have,

$$t_{1/3}=\frac{2.303 log(3/2)}{k}$$

$$=\frac{0.403}{0.0374}$$

$$= 10.8 \text{ minutes}$$

(b) Substitution of $a = 1.00$ and $x = 0.80$ in equation (12.22) yields

$$k=\frac{2.303}{t}log\frac{1.00}{(1.00-0.80)}$$

$$=\frac{1.6098}{t}$$

$$t=\frac{1.6098}{0.0374}=43.0 \text{ minutes}$$

(c) Second-order Reactions

For second-order reactions two possibilities exist for single-step reaction:

$$Type\,1: \quad A\rightarrow Products$$

$$Type\,2: \quad A+B\rightarrow Products$$

For Type 1 reactions the rate law is

$$-\frac{dc}{dt}=kc^2 \tag{12.29}$$

where c is the concentration of the reactant. Integration of equation (12.29) without limits give,

$$\frac{1}{c} = kt + C \qquad (12.30)$$

where C is a constant of integration. At $t = 0$, $c = c_0$. Upon substitution in equation (12.30) and rearranging we get,

$$\frac{1}{c} = kt + \frac{1}{c_0} \qquad (12.31)$$

This also is an equation of a straight line and a plot of $\frac{1}{c}$ vs t should give a straight line (Figure 12.12) with a slope equal to k. So k of such a second-order reaction can be determined from the graph.

An example of such a reaction is the decomposition of nitrogen dioxide at moderately high temperature (300 to 400°C).

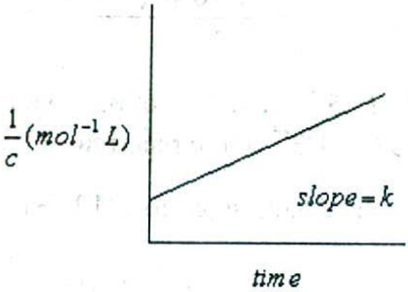


Figure 12.12 Plot of $\frac{1}{c}(mol^{-1} L)$ vs *time* for second-order reaction

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

Example 12.6: At 330°C measurements of the concentrations of NO_2 at various times gave the following data:

Time (s)	0	60	120	180	240	300	360
$[NO_2]$ mol $L^{-1} \times 10^2$	1.00	0.683	0.518	0.418	0.350	0.301	0.264
$1/[NO_2]$	100	146	193	239	286	332	379

Use a graphical method (a) to show that the reaction is of second order and (b) find the rate constant k for the reaction.

Solution: To make a plot according to Equation (12.31) the reciprocal of concentrations have to be calculated. These are shown above as part of the data. Figure 12.13 shows the plot of $1/[NO_2]$ versus time in seconds. It can be seen that the graph is a straight line. This indicates that the reaction is second order. The gradient of the line is k.

$$k = \frac{200}{250} = 0.80\, L\, mol^{-1} s^{-1}$$

Half-life of second-order reaction

The expression for half life of the second order reaction can be deduced by substituting (1/2) c_o for c in equation (12.31) which takes the form

$$k\,t_{½} = \frac{1}{(1/2)c_0} - \frac{1}{c_0} = \frac{2}{c_0} - \frac{1}{c_0} = \frac{1}{c_0}$$

and $$t_{½} = \frac{1}{kc_0} \qquad (12.32)$$

The half life of a second-order reaction is inversely proportional to the initial concentration.

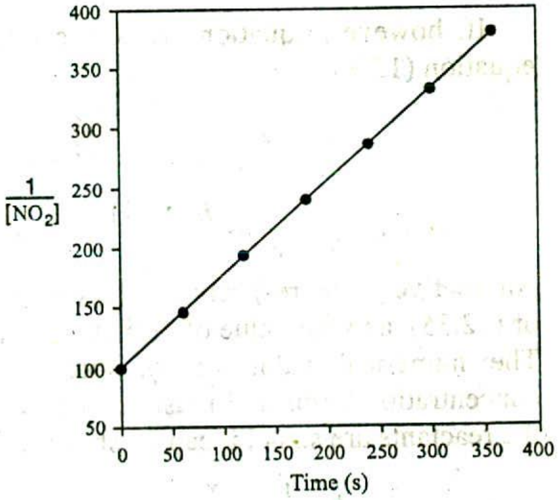


Figure 12.13 Plot of $\frac{1}{[NO_2]}$ vs time

Example 12.7: Use the value of k for the reaction in Example 12.6 to find its half-life.

Solution: Substitution of the values of k and c_o in Equation 12.32 gives

$$t_{½} = \frac{1}{k\,c_0} = \frac{1}{(0.80)\times 1} = 1.25 \text{ s}$$

For a second-order reaction of the Type 2

$A + B \rightarrow$ Products, the rate equation is

$$-\frac{d(a-x)}{dt} = k_2(a-x)(b-x) \qquad (12.33)$$

where a and b are the initial concentrations of the reactants A and B respectively and x is the mol L^{-1} of each reactant reacted. This equation may be solved by using the method of partial fraction. Integration without limits takes the form,

$$\frac{1}{(a-b)} ln\frac{a-x}{b-x} = k_2 t + C \qquad (12.34)$$

where, at $t = 0$, $x = 0$ and $C = \frac{1}{(a-b)} ln\frac{a}{b}$

A plot of $\frac{1}{(a-b)} ln\,\frac{a-x}{b-x}$ *vs* t yields a straight with slope k_2 and intercept. $\frac{1}{(a-b)} ln\frac{a}{b}$

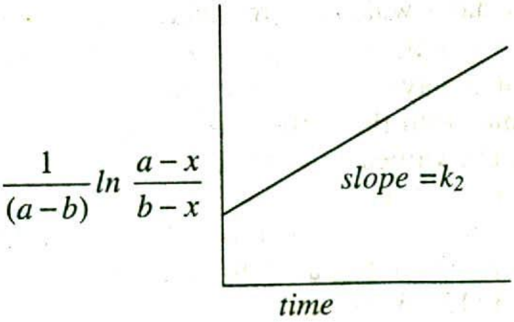


Figure 12.14 Plot of $\frac{1}{(a-b)} ln\,\frac{a-x}{b-x}$ vs *time*

If, however, equation (12.33) is integrated within limits at $t = 0, x = 0$, we get equation (12.35)

$$k_2 t = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} \tag{12.35}$$

A plot of $\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$ *vs* t will yield a straight line of slope equal to k_2. Alternatively, the respective values of a, b, x and t may be inserted in equation (12.34) or (12.35) and the value of k_2 may be obtained. k_2 has the dimension of time $^{-1}$ conc^{-1} . The numerical value of k_2, therefore, depends on the unit of expressing the concentration terms and must be clearly mentioned. If, however, the concentrations of the reactants are same, it can be shown that,

$$k = \frac{1}{at} \cdot \frac{x}{(a-x)} \tag{12.36}$$

Half-life of a second order-reaction

At $t_{1/2}$, $x = \frac{a}{2}$ which upon substitution in equation (12.36) gives,

$$t_{1/2} = \frac{1}{ak}$$

In other words $t_{1/2}$ for a second-order reaction is proportional to $\frac{1}{a}$.

12.6.3 Determination of order of reactions : a summary

A number of methods are known for the determination of the order of reactions.

(1) Initial rate method: Example of this method has been given in *Section 12.6* . In this method the rate law is established, which gives the order with respect to the reactants which control the rate of the reaction.

(2) Method of integration: The order of a reaction is often determined, though not always wisely, by fitting the experimental data of concentration at different times into the different rate equations and noting the best constancy thus obtained in the values of k. If the first-order expression gives the constant values of k, the order is 1 and if the second order rate expression yields the constant value of k the order is 2. This method of trial and error is known as the method of integration since the integrated form of the rate expression, e.g., equations (12.21), (12.31) and (12.35) are used.

The method is only of limited accuracy and may give rise to misleading results if the reaction is a complex one. Also reactions of fractional order cannot be properly dealt with by this method.

(3) Graphical method: For reactions of the type: A → Products, the order of the reaction may be determined by examining whether the data fits one of the graphical representations of the integrated rate equations. If the data fit one of the graphical representations shown in Figures (12.6) and (12.7) then the reaction is first-order.

On the other hand, if the data fit the graph shown in Figures (12.11) or (12.13) it is a second-order reaction.

(3) Differential method: The rate of a reaction of which the order is n is given by

$$\text{rate} = k\,c^n$$

$$\text{or} \quad \log\,(\text{rate}) = \log k + n \log c \quad (12.37)$$

So that a plot *log* (rate) *vs* *log c* would yield a straight line of slope n and intercept *log k*. Thus both the order and the specific reaction rate can be determined as shown in Figure 12.15.

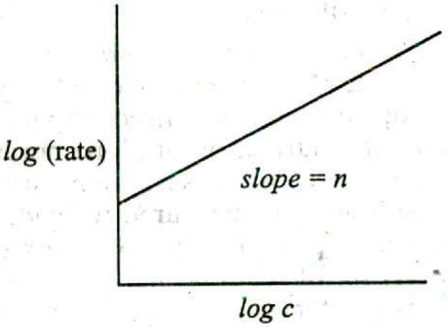


Figure 12.15 A plot of *log* (rate) vs *log c*

The order may be calculated simply from measurements of the rate of the reaction at two different concentrations. For this purpose in the plot of c vs time, tangents are drawn at two concentrations c_1 and c_2. The slopes of these tangents, $-dc_1/dt$ and $-dc_2/dt$ at these points, represent the rates at concentrations c_1 and c_2 respectively. If the order of the reaction is n then use of equation (12.37) gives

$$n = \frac{\log(-dc_1/dt) - \log(-dc_2/dt)}{\log c_1 - \log c_2} \qquad (12.38)$$

This method has an additional advantage.The initial rate of the reaction can be estimated by extrapolation. After doing this for a series of initial concentrations a plot of *log (initial concentration)* vs *log (initial rate)* should yield a straight line, the slope representing the order. From a comparison of the orders so obtained useful and significant information can be obtained regarding complexities of the reaction.

(4) Isolation method: The differential method can be extended to the evaluation of the order with respect to more than one reactant. If the reaction is of mth order with respect to A and nth order with respect to B, then, the rate law is given by equation (12.7),

$$\text{rate} = k\,c_A^m\,c_B^n$$

so that the total order is $(m + n)$. If the concentration of one of the reactants, say A, is kept quite large with comparison to B, the concentration of A will remain practically unaltered during the course of the reaction and the order now determined will be with respect to B only. Next B is taken in large excess and the order with respect to A is determined. Thus from the values of n and m so obtained the total order may be computed. This method is known as *the isolation method*. In principle the method is similar to the initial rate method. The method has been illustrated in Examples 12.2 and 12.3.

(5) Method using half-life of the reaction: Equation (12.26) shows that the half-life of a first order reaction is independent of the reactant concentration. Again according to equation (12.32) for a second order reaction the half-life is inversely proportional to the initial concentration of the reactant. The half-life of the reaction under consideration is determined at different concentrations. Inspection of the values for different concentrations will reveal whether the reaction is first order or second order with respect to the reactant.

(6) Guggenheims method: This method is of wide application for reactions of first order and yields accurate values. The method is used when concentrations cannot be measured directly but a property (such as conductivity, rotation of the plane of polarization of plane polarized light as measured by a polarimeter, pressure in the case of gases, intensity of absorption of radiation etc) related to concentration is measured instead. Let r_1, r_2, r_3 etc. be the readings of any parameter (property) proportional to the extent of reaction taken at times t_1, t_2, t_3 etc. and a second set of reading: r'_1, r'_2, r'_3 etc. taken at (t_1+T), (t_2+T), (t_3+T) etc., where T is the time interval between the start of the first and the second set of readings. For the nth reading of each set

$$2.303\ log\ (r'_n - r_n) = constant - k\ t_n,$$

such that a plot of $log\ (r'_n - r_n)\ vs\ t_n$ will give a straight line of $slope = -\dfrac{k}{2{\cdot}303}$. An example of this type of treatment will be discussed in detail later (*Section 12.7*). Any parameter that is proportional to the concentration can be used in this method. The above procedure, known as *Guggenheim's method*, is based on equation (12.21). The time interval between readings of r'_n and r_n should be about 2 to 3 times the $t_{1/2}$.

12.7 Some Typical Reactions

(a) First-order reaction: (i) The thermal decomposition of nitrogen pentoxide in

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$$

the gas phase and also in solution is an excellent example of a first order reaction. The reaction has been studied extensively and it has been found to obey first-order kinetics strictly over a wide range of concentration and temperature. The reaction also proceeds in CCl_4 solution and the N_2O_4 remains in solution whereas oxygen is liberated and goes out as gas due to its very low solubility in carbon tetrachloride. The reaction, therefore, can be easily followed by measuring the volume of oxygen liberated at measured time intervals. In this case the rate expression becomes

$$k = \frac{2.303}{(t_2 - t_1)} log\ \frac{V_\infty - V_1}{V_\infty - V_2} \tag{12.39}$$

where V_∞ is the volume of oxygen evolved after infinite time, V_1 and V_2 are the volumes of oxygen evolved at time t_1 and t_2, as $V_\infty - V$ is proportional to concentration of N_2O_5 in CCl_4.

Table 12.1 Decomposition of N_2O_5 in CCl_4 at 30°C

Time (sec. $\times 10^{-3}$)	0	2.4	4.8	7.2	12.0	16.8	19.2
$(V_\infty - V)$	84.8	59.2	57.2	47.2	32.2	21.9	18.0

k (mean value) = 8.1×10^{-5} sec^{-1}

Alternatively *log c*, where *c* is the concentration, can be plotted against time and *k* can be evaluated from the slope of the straight line.

The decomposition of the pentoxide in gas phase is somewhat complicated due to the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

Table 12.2. Decomposition of N_2O_5 in CCl_4 at 45°C.

Time sec.	$[N_2O_5] = c$ mol L^{-1}	log c
0	2·33	0·367
184	2·08	0·318
319	1·91	0·281
526	1·67	0·223
1198	1·11	0·045
1877	0·72	– 0·142

k (mean value) = 6.2×10^{-2}sec^{-1}

The data in Table 12.2 on the same reaction when properly plotted yields a straight line as shown in Figure 12.16.

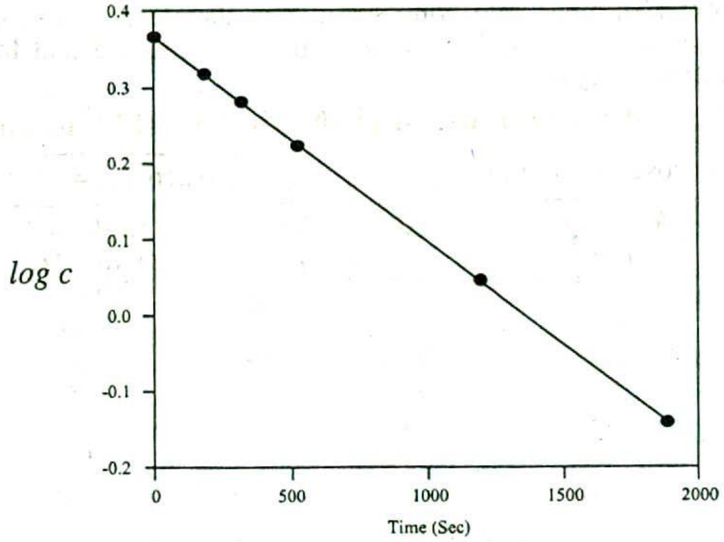


Figure 12.16 Plot of *log c vs* time according to data in Table 12.2.

(ii) Hydrolysis of cane sugar (sucrose) to glucose and fructose catalyzed by acid follows first order kinetics.

$$\underset{\textit{sucrose}}{C_{12}H_{22}O_{11}} + H_2O + (H^+) \rightarrow \underset{\textit{glucose}}{C_6H_{12}O_6} + \underset{\textit{fructose}}{C_6H_{12}O_6} + (H^+)$$

Since sucrose is optically active and dextrorotatory and an equimolar mixture of glucose and fructose is laevorotatory, the optical rotation of plane of plane polarized light will change during the progress of the above reaction. Consequently, the reaction rate can be conveniently followed by measuring the angle of rotation of the plane of polarization of plane polarized light at suitable time intervals.

Let, α_0 be the angle of rotation initially

α_t be the angle of rotation at time *t*

α_∞ be the angle of rotation at infinite time (say after 72 hours)

Then, $(\alpha_0 - \alpha_\infty)$ is proportional to initial concentration and $(\alpha_0 - \alpha_t)$ is proportional to the concentration at time *t*

Therefore $[\alpha_0 - \alpha_\infty - (\alpha_0 - \alpha_t)] = (\alpha_t - \alpha_\infty)$ is proportional to the concentration remaining unreacted at time *t*, i.e. *(a – x)*.

These data when substituted in equation (12.22) yield

$$k = \frac{2.303}{t}\log\frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \qquad (12.40)$$

Results shown in Table 12.3 show the constancy of the values of *k* so obtained over a wide concentration change. The specific reaction rate is also independent of initial concentration of the sugar. In this case the concentration of water (although it is a reactant) does not enter into the rate expression involving the two reactant species due to its presence in large excess in the reaction mixture. Such a reaction in which one reactant does not enter into the rate equation due to its presence in large excess is sometimes called *pseudo-unimolecular reaction*. It is to be noted that the acid in the reaction mixture acts as catalyst.

Table 12.3: Hydrolysis of sucrose at 30°C in 2.5 mol L^{-1} formic acid

Initial [sucrose] =0·44 mol L^{-1}			Initial [sucrose] =0·167 mol L^{-1}		
Time (hour)	*Angle of Rotation(α)*	$k \times 10^2$	*Time (hour)*	*Angle of Rotation (α)*	$k \times 10^2$
0	57·9		0	22·1	–
2	53·2	3·32	5	17·8	3·38
6	44·4	3·39	15	11·1	3·39
18	25·2	3·28	30	4·5	3·38
27	13·5	3.44	59	−1·8	3·41
40	3·4	3·39	133	−5·1	3·20
66	−7·45	3·37	∝	− 5·5	
∝	−15·45	–			

Experimental data of this reaction can also be treated in a different manner by using the Guggenheim method of calculation. In this method α_0 and α_∞ need not be known.

Guggenheim Method

Let us consider that, $\alpha_1, \alpha_2, \alpha_3 \cdots\cdots\cdots \alpha_n$ are the angles of rotation at times t_1, t_2, t_3 -----t_n respectively and α_1', α_2', α_3' .... α_n' be the angles of rotation at times $(t_1+T), (t_2+T), (t_3+T) \cdots\cdots (t_n+T)$ where T is a constant difference (*Section 12.6.3*). Now, if α_0 is the angle of rotation at $t = 0$, then for a first-order reaction we can write the following expressions for t_1 and $(t_1 + T)$ (Equation 12.25):

$$(\alpha_0 - \alpha_1) = \alpha_0 e^{-kt_1} \tag{12.41}$$

and

$$(\alpha_0 - \alpha_1') = \alpha_0 e^{-k(t_1+T)} \tag{12.42}$$

Subtractiong equation (12.42) from (12.41) we get,

$$(\alpha_1' - \alpha_1) = \alpha_0 e^{-kt_1}(1 - e^{-kT}) \tag{12.43}$$

Taking logarithm on both sides of equation (12.43),

$$ln(\alpha_1' - \alpha_1) = -kt_1 + ln\, \alpha_0 e^{-kT} \tag{12.44}$$

or

$$ln(\alpha_1' - \alpha_1) = -kt_1 + \text{ constant, since } \alpha_0 e^{-kT} \text{ constant} \tag{12.45}$$

Similarly for the *n*th reading at t_n and (t_n+T) we can write,

$$ln(\alpha_n' - \alpha_n) = -kt_n + \text{constant}$$

since α_0 and T are constants. According to equation (12.45), a plot of $ln(\alpha_1' - \alpha_1)$ versus t_1 gives a straight line with slope $-k$ (Figure 12.17).

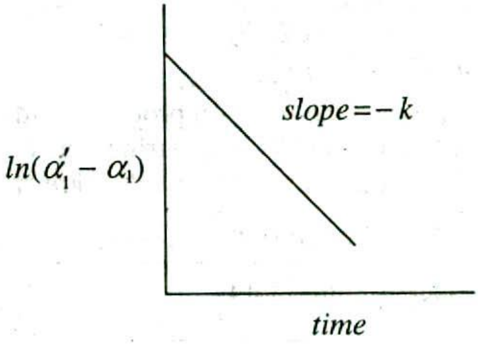


Figure 12.17 A plot of $ln(\alpha_1' - \alpha_1)$ vs *time* according to Guggenheim Method

The data in Table 12.4 serve as an example.

Table 12.4 Hydrolysis of sucrose in (≈1.0 mol L^{-1}) HCl solution at 28°C

Time(min.)	α	$(\alpha_n - \alpha'_n)$
3	12.7	6.9
5	11.4	6.0
7	10.4	5.56
9	9.6	5.25
12	8.5	4.85
16	7.3	4.4
18	6.7	4.1
20	6.1	3.3
22	5.6	3.68
24	5.1	3.6
26	4.6	3.4
28	4.1	3.3
30	3.6	3.1

(iii) Hydrolysis of several esters, e.g., methyl and ethyl acetate, catalyzed by acids are examples of first order reactions in solutions. The thermal decomposition of PH_3 to P_4 and H_2 is a gaseous first-order reaction although the reaction is heterogeneous to some extent. The decomposition of azomethane to C_2H_6 and N_2 is a good example of first- order gas phase reaction :

$$\begin{array}{cccccc} CH_3N = NCH_3 & \rightarrow & C_2H_6 & + & N_2 \\ \text{Azomethane} & & \text{ethane} & & \text{nitrogen} \end{array}$$

(b) Second order reaction: (i) Formation of $COCl_2$ from CO and Cl_2 according to the equation

$$\begin{array}{ccccc} CO & + & Cl_2 & \rightarrow & COCl_2 \\ 1\ vol & & 1\ vol & & 1\ vol \end{array}$$

is a second order gaseous reaction. Since the reaction proceeds with a change in volume the extent of the reaction can be followed by measuring the change in pressure at constant volume and constant temperature. Some kinetic data are shown in Table 12.5.

Table 12.5 Formation of $COCl_2$

Time/min.	Concentration/mol L^{-1}		$k\left(=\frac{1}{at}\cdot\frac{x}{a-x}\right)\times 10^3$
	CO	$COCl_2$	
0	0·500	–	–
6	0·488	0·0115	7·8
12	0·479	0·0203	7·1
24	0·463	0·0371	6·8
36	0·447	0·0528	6·5

The slight deviation in the values of k indicates complex mechanism of the reaction.

(ii) Hydrolysis of several esters of the aliphatic series in alkaline aqueous medium obey strictly second order law. (*Note that hydrolysis of esters in acid medium is kinetically of the first- order*). Ethyl acetate is hydrolysed as follows :

$$CH_3COOC_2H_5(aq) + NaOH\,(aq) \rightarrow CH_3COONa(aq) + C_2H_5OH(aq)$$

The acetic acid formed as a result of hydrolysis instantaneously reacts with $NaOH$ to form sodium acetate. The reaction can be followed by measuring quantitatively the amount of $NaOH$ left unreacted by titrating against a standard acid solution. A more convenient method of following this reaction is to measure the electrical conductance as a function of time. Since as a result of the reaction highly mobile hydroxyl ions are replaced by less mobile acetate ions, the conductance falls as the reaction proceeds. If the initial concentrations of $NaOH$ and ethyl acetate are the same, equation (12.36) can be used. Introducing the conductance in the rate expression when C_t and C_o are respectively the conductance at time t and at zero times and a is the initial concentration one can see that,

$$a \propto (C_0 - C_\infty)\text{and } x \propto (C_0 - C_t)$$

That means, $(a-x) = C_t - C_\infty$. Upon substitution of these in equation (12.36) we get,

$$k = \frac{1}{at}\cdot\frac{C_0 - C_t}{C_t - C_\infty} \qquad (12.46)$$

Rearranging equation (12.46) we get,

$$C_t = \frac{1}{ak}\cdot\frac{C_0 - C_t}{t} + C_\infty \qquad (12.47)$$

A plot of C_t vs $\frac{C_0 - C_t}{t}$ would yield a straight line of slope $= \frac{1}{ak}$ (Figure 12.18).

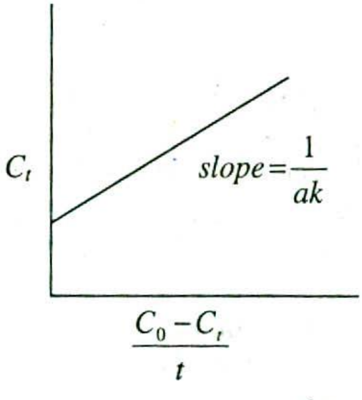


Figure 12.18 A plot of C_t vs $\left(\frac{C_0 - C_t}{t}\right)$

In Table 12.6 such data are included and a linear plot according to equation (12.47) can be obtained.

Table 12·6 Hydrolysis of ethyl acetate by *NaOH* at 32°C
$[NaOH] = 0.01$ mol L^{-1} and $[EtAc] = 0.01$ mol L^{-1}

Time (minites)	Conductance × 10^4 (Ω^{-1})	$\frac{(C_0 - C_t)\times 10^3}{t}$
5	3.45	2.1
10	3.00	1.5
15	2.75	1.17
25	2.47	0.81
35	2.33	0.65
45	2.23	0.52
55	2.07	0.44
70	2.15	0.35

$k = 12.7$ L mole^{-1} min^{-1}

(iii) The conversion of ammonium cyanate to urea, an isomeric change, is a second - order process although it involves only one molecule.

(c) *Higher order reactions*: The number of third order reactions is few, while reactions of higher order are practically unknown. The reaction $2NO + Cl_2 \rightarrow 2NOCl$ takes place in the gaseous phase with a decrease in volume and it has been kinetically studied by observing the change of pressure as a function of time. Over a wide range of temperature and pressure the reaction has been found to be third-order. Similar procedure for the reaction $2NO + O_2 \rightarrow 2NO_2$ established it to be third-order. The reaction between NO and Br_2 giving $NOBr$ is also a third-order reaction.

12.8 Complex Reactions

Most reactions are not as simple as described above. Complexities may arise as other reactions involving the products of a simple reaction which makes the study of kinetics of such reactions complicated. Brief discussions of some complex reactions are given here.

12.8.1 Reversible reactions

A number of reactions, both in solution and in the gas phase, are reversible, i.e., the forward reaction is opposed by the reverse reaction. Such reactions are special type of simultaneous reactions. Consequently, in the treatment of kinetic data the factors due to the reverse reaction must be considered. In reversible reactions a number of possibilities arise and for the sake of brevity a summary table is given below for the various possibilities

Table 12.7 Rate expressions for opposing reactions

System	Nature of reaction	Integrated rate expression
1. $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$	First-order reaction opposed by a first-order reaction.	$k_1 = \frac{x_e}{at} \ln \frac{x_e}{x_e - x}$
2. $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C$	First-order process opposed by a second-order reaction.	$k_1 = \frac{x_e}{t(2a - x_e)} \ln \frac{ax_e + x(a - x_e)}{x(x_e - x)}$
3. $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$	Second-order process opposed by a first-order reaction.	$k_1 = \frac{x_e}{t(a^2 - x_e^2)} \ln \frac{x_e(a^2 - x.x_e)}{a^2(x_e - x)}$
3. $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$	Second-order reaction opposed by a second-order one.	$k_1 = \frac{x_e}{2ta(a - x)} \ln \frac{x(a - 2x_e) + ax_e}{a(x_e - x)}$

In Table 12.7, x_e corresponds to the concentration of a suitable product at equilibrium and all a terms correspond to the initial concentration and x is the concentration of the product at any time t.

Examples of reactions from 1 to 4 in Table 12.7 are

(1) mutarotation of π-bromonitrocamphor in chloroform solution,

(2) decomposition of certain alkyl ammonium halide to a tertiary amine and an alkyl halide in solution, thermal decomposition of ethyl bromide in gas phase,

(3) isomerisation of alkyl ammonium cyanate to the corresponding substituted urea in aqueous solution,

(4) decomposition or the formation of hydrogen iodide respectively.

12.8.2 Consecutive reactions

Another common type of simultaneous reaction is consecutive reaction. Many reactions which appear from a cursory glance to be simple are really consecutive reactions. In this type of reaction an intermediate product is formed first; this intermediate product then breaks down or is converted to the final products. Such a reaction can be represented as follows:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The variations of the concentrations of A, B and C are schematically shown in Figure 12.19. At the start of the reaction $[B]$ and $[C]$ are zero. As time passes B is formed which in turn is transformed to C. Since at the beginning of the reaction the amount of

B formed is quite small, the rate of formation of C is also small. This portion is shown by p in the figure. With the progress of the reaction more B is formed and the rate of the reaction increases. After the point q is reached concentration of B falls off as indicated. Such reactions always will show a very slow rate at the beginning which is subsequently followed by more rapid rate. The time period over which the reaction is very slow is known as the *induction period*, shown in Figure 12.19 as t_I.

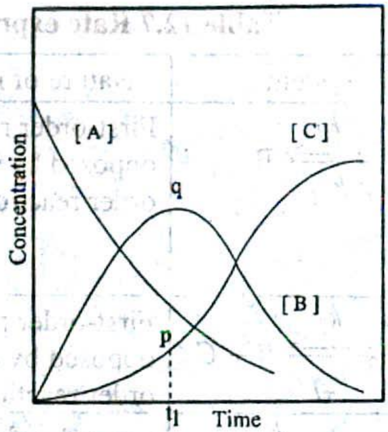


Figure 12.19 Variation of the concentrations of A, B and C with time in consecutive reaction.

The position of the maximum and its magnitude is controlled by the relative values of k_1 and k_2.

The overall rate of the reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

can be shown as

$$-\frac{d[A]}{dt} = k_I\,[A] \tag{12.48}$$

The rate of formation of B is given by

$$\frac{d[B]}{dt} = k_I\,[A] - k_2\,[B] \tag{12.49}$$

and that of C is

$$\frac{d[C]}{dt} = k_2\,[B] \tag{12.50}$$

Now

$$-\frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} = 0 \tag{12.51}$$

Complete solutions of the above equations finally give the relationships

$$[B] = [A]_0\,\frac{k_I}{k_2 - k_I}\,(e^{-k_I t} - e^{-k_2 t}) \tag{12.52}$$

$$[C] = [A]_0\left\{1 - \frac{k_2\,e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\right\} \tag{12.53}$$

and

$$[A] = [A]_0\,e^{-k_1 t} \tag{12,54}$$

where $[A]_0$ is the initial concentration of A.

The decomposition of H_2O_2 by HBr is an example of this type.

$$H_2O_2 + H^+ + Br^- \rightarrow HBrO + H_2O$$
$$H_2O_2 + HBrO \rightarrow H_2O + O_2 + H^+ + Br^-$$

This is, however, a case where the HBr is regenerated in the second step and, therefore, HBr acts as a catalyst. A better example is the oxidation of arsenious acid by iodine:

$$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2I^-$$

The suggested mechanism from kinetic study shows the reaction to proceed step wise :

$$I_2 + H_2O \rightarrow HIO + H^+ + I^-$$
$$HIO + H_3AsO_3 \rightarrow H_3AsO_4 + H^+ + I^-$$

However, the mechanisms of many consecutive reactions are more complex and not clearly understood.

12.9 Influence of Temperature on Reaction Rates

As noted earlier, the rate of a reaction is affected by temperature. The general effect of temperature on reaction rate is that in almost all cases an increase of temperature brings about an increase in the reaction rate. This shows up in the values of rate constants k (in rate laws) which is found to increase with the increase in temperature. The increase in the rate with increase in temperature is different for different reactions but an empirical fact is that the rate becomes approximately *double for each 10°C rise in temperature* when the temperature is not much different from the room temperature.

A quantitative expression for temperature dependence of reaction rate constants was proposed by S. Arrhenius in 1889. For most reactions the dependence could be expressed by the equation

$$k = A e^{-E_a/RT} \qquad (12.55)$$

In this equation, called the *Arrhenius equation*, e is the base of the natural logarithm scale, E_a is the activation energy, R is the gas constant and T is the temperature in degree Kelvin. A in the Arrhenius equation, which is assumed to be a constant for a particular reaction, is called the *frequency factor*. The frequency factor is related to the frequency of collision with proper orientation. (In fact A has a slight dependence on temperature).

Taking the natural logarithm of both sides of equation (12.55) one obtains

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (12.56)$$

Converting from natural log to log to the base 10 equation (12.56) takes the form

$$\log k = \log A - \frac{E_a}{2.303\, RT} \qquad (12.57)$$

Equation (12.57) is in the form of an equation of a straight line, $y = mx + c$, in which one variable y is *log k* and the other x is *1/T*. If *log k* is plotted against *1/T* one obtains a straight line with the slope $= -E_a/2.303R$. The activation energy E_a can be calculated from the value of the slope. The intercept is *log A* from which the frequency factor *A* may be calculated.

Some data for the decomposition of N_2O_5 at various temperatures are given in Table 12.8. The data plotted in Figure 12.20 give a straight line as predicted by the Arrhenius equation.

Table 12.8 Rate constants for decomposition of N_2O_5 at different temperatures

Temperature (K)	Rate constant (s^{-1})
283	3.83×10^{-6}
293	1.71×10^{-5}
303	6.94×10^{-5}
313	2.57×10^{-4}
323	8.78×10^{-4}

Slope $= -5667 = -E_a/2.303R$

The value of E_a calculated from the slope $= 108.5 \text{ kJ mol}^{-1}$

An approximate value of the activation energy may be obtained by determining the values of the rate constants, k_1 and k_2, at two different temperatures T_1 and T_2 respectively and writing two equations as follows:

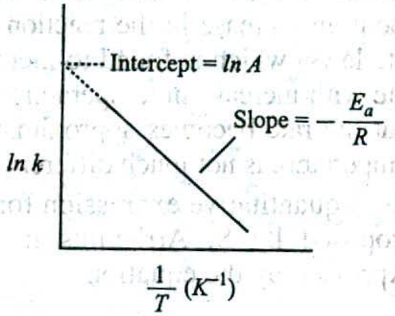


Figure 12.20 Plot of *ln k vs 1/T*

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \tag{12.58}$$

$$\log k_2 = \log A - \frac{E_a}{2.303\,RT_2} \tag{12.59}$$

Eliminating *log A* from the two equations one obtains

$$\log k_2 - \log k_1 = -\frac{E_a}{2.303\,RT_2} + \frac{E_a}{2.303\,RT_1} \tag{12.60}$$

or

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12.61}$$

Example12.8: The rate of a chemical reaction at 310 K is double of that at 300 K. Calculate the energy of activation of the reaction.

Solution: At T_1 = 300 K let the rate constant be k_1. Then at T_2 = 310 K the rate constant will be $2k_1$. Substituting these data in equation (12.61) we get,

$$log\frac{2k_1}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{300}-\frac{1}{310}\right)$$

Upon solving we get, E_a = 53.60 kJ mol^{-1}.

12.10 Collision Theory of Reaction Rates

In trying to understand the effect of temperature on the rate of reaction it should be recognized that a chemical reaction is only a rearrangement of chemical bonds among the atoms in the reacting system. For such a rearrangement to be effective the reacting molecules must come in contact or a collision between the molecules must take place.

Arrhenius argued that if collision between reactant molecules is a necessary condition for reaction, the rate of reaction should be equal to the frequency of collisions (*Section 2.21*). Calculations, however, show that the rates of most reactions are much smaller than the frequency of collisions. Again, the increase of temperature by 10°C results in only a 2% – 3% increase in the frequency of collisions, but the reaction rate increases 200% to 300%. This means that all collisions between reacting molecules do not lead to reaction. The question one may ask is '*which collisions lead to reaction*'? To answer this question Arrhenius suggested that only '*active*' molecules can take part in a reaction. These 'active' molecules have energies in excess of those possessed by the normal molecules. *The minimum extra energy per mole in excess of the average energy which enables the molecules to undergo reaction was termed the activation energy,* E_a.

The number of molecules having energies larger than a value E_a may be obtained from the Maxwell-Boltzmann distribution equation (*Section 2.16*), e.g.

$$\frac{\text{Number of molecules having energy larger than } E_a}{\text{Total number of molecules}} = e^{-E_a/RT} \qquad (12.62)$$

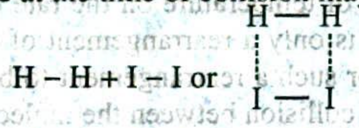
If all collisions between active molecules lead to reaction the rate of the reaction should be equal to the product of the frequency of collisions and the fraction of molecules which have energies equal to or in excess of E_a. An increase of temperature results in a sharp increase in the number of molecules having energy larger than a given value so that the effects of temperature on reaction rates become understandable. If the total number of collisions per second in a gas at unit concentration is Z (known as collision frequency), the number of molecules undergoing reaction in unit volume per second, which is equal to the velocity constant k, will be given by

$$k = Z\,e^{-E_a/RT} \qquad (12.63)$$

Thus the collision theory leads to a means of calculating reaction rates from molecular collision frequency. Although in a few cases agreement between the calculated and observed values of specific reaction rates has been found, disagreement is more numerous. This suggests that *all collisions between active molecules do not lead to reaction.* To account for this discrepancy it was necessary to rewrite equation (12.63) in the form,

$$k = P\,Z\,e^{-E_a/RT} \tag{12.64}$$

where P is called the *steric factor (also called probability factor or geometric factor)* and is related to the proper orientation of the active molecules at the time of collision. This factor is independent of temperature changes. The following figures for the reaction between hydrogen and iodine to produce hydrogen iodide will show how the orientation of the molecule at the time of collision may affect the rate of the reaction.



$$H-H + I-I \text{ or } \begin{array}{c} H-H \\ \vdots \quad \vdots \\ I-I \end{array}$$

As can be seen from the above reaction between H_2 and I_2, the two reactants must align (orient or line-up) properly for the reaction to take place, However, as the reactant molecules become more complicated, the activated complex becomes more difficult to visualize. Originally P was supposed to measure the geometric requirements that must be met if collisions between two active molecules were to result in reaction. It is possible that many other factors may affect P, and it is a measure of the discrepancy between the experimental results and the results predicted by the collision theory. For ordinary thermal reactions the value of P ranges from 10^{-2} to 10^{-6} depending on the nature of the reaction.

12.11 Transition State Theory

It is now believed that all chemical processes proceed through the formation of an intermediate *activated complex or transition state.* The activated complex is a grouping of atoms of reactant molecules which is unstable. The activated complex breaks up or decompeses at a definite rate to give the products of the reaction. Consider a reaction of the type

$$AB + C \rightarrow AC + B$$

It is thought that at first an activated complex, having a structure intermediate between that of the reactants and products, is formed. In the above example the reaction may be written as

$$AB + C \rightarrow \underset{\textit{Activated complex}}{A\cdots B\cdots C} \rightarrow AC + B$$

The activated complex $(A\cdots B\cdots C)$ has a higher potential energy than either the reactants or products. The change of potential energy with 'progress' of the reaction, i.e., the reaction co-ordinate is diagrammatically represented in Figure 12.21.

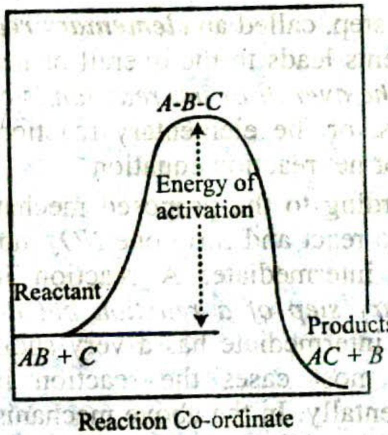
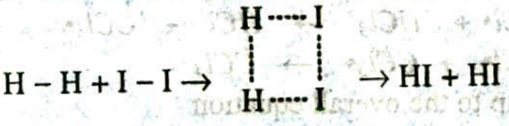


Figure 12.21 Potential energy as a function of reaction co-ordinate

The difference in energy between $AB + C$ and the activated complex is equal to E_a, the energy of activation of the reaction, as shown in equation (12.55). It is to be noted that to get from the reactant side to the product side the system has to cross over an energy barrier corresponding to the energy of the activated complex.

In spite of collision between molecules reaction cannot take place unless the energy barrier can be crossed. The difference between the energy of the reactants and that of the products is the *enthalpy change of the reaction* (ΔH). As the energy level of the products is lower than that of the reactants, energy is given out during the reaction, the reaction being exothermic. In endothermic reactions the energy level of products is between that of the reactants and the activated complex.

A proper understanding of the activated complex needs careful study and imagination. In the case of the reaction between hydrogen and iodine to form hydrogen iodide the activated complex has been represented as below:



$$H-H+I-I \rightarrow \begin{array}{c} H\cdots I \\ \vdots\quad\;\vdots \\ H\cdots I \end{array} \rightarrow HI + HI$$

Activated complex

As the reactant molecules become more complicated the activated complex becomes more difficult to visualise.

12.12 The Rate Law and Mechanism of Reaction

It has been stated before that for a reaction to take place reacting molecules must collide with each other. Remembering that chemical reactions involve breaking and forming of bonds it is hard to imagine that these breaking and forming of bonds always take place instantaneously and in one step. It is believed that in most reactions more than one step is involved in the formation of the products from the reactants. Such speculations are arrived at by bringing together both theory and experiment. Take for example the simple reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g) \qquad \text{(overall reaction)}$$

The reaction is experimentally found to be of second-order. This gas phase reaction is believed to take place in two steps:

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g) \qquad \text{(elementary reaction)}$$
$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \qquad \text{(elementary reaction)}$$

Each step, called an ***elementary reaction***, is a *single molecular event*. A sequence of such events leads to the overall or net reaction. *The set of elementary reactions which lead to the overall or net reaction is called the* ***mechanism of the reaction***. The sum of the steps, or the elementary reaction equations, in the mechanism should yield the overall or net reaction equation.

According to the proposed mechanism for the above reaction two NO_2 molecules collide to react and form one NO_3 molecule and one NO molecule. NO_3 is said to be a reaction intermediate. A reaction intermediate *is a species produced during an elementary step of a reaction but does not appear in the net reaction equation.* A reaction intermediate has a very short life and takes part in the subsequent step very fast. In most cases the reaction intermediate cannot be isolated and identified experimentally. In the above mechanism NO_3 is the reaction intermediate, which reacts quickly with CO to produce NO_2 and CO_2. One can see that by adding the above two elementary reaction equations the overall equation is obtained.

Let us consider the following example:

Carbon tetrachloride is obtained by the chlorination of chloroform, $CHCl_3$.

$$Cl_2 + CHCl_3 \rightarrow CCl_4 + HCl$$

The following elementary steps have been proposed to constitute the mechanism of this gas phase reaction.

$$Cl_2 \rightleftharpoons 2Cl\bullet$$

$$Cl\bullet + CHCl_3 \rightarrow HCl + CCl_3\bullet$$

$$Cl\bullet + CCl_3\bullet \rightarrow CCl_4$$

These equations add up to the overall equation

12.13 Molecularity and Order of Reactions

The molecularity *is the number of particles (molecules, atoms or ions) on the reactant side of an elementary reaction.* We do not talk of molecularity of a net or overall reaction. Molecularity is not related to the stoichiometric equation of a reaction.

A unimolecular *reaction is an elementary reaction that involves one reactant particle.*

Example: $Cl_2 \rightarrow 2Cl$

Maleic acid → Fumaric acid

Cyclopropane → Propene

A bimolecular *reaction is an elementary reaction which involves two reactant particles.*

Example: $C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$

Bimolecular reactions are the most common. *An elementary reaction that involves three reactant species, i.e.,* a termolecular *reaction,* is less common as the possibility of three particles colliding together in proper orientation is small.

Example: $2NO\,(g) + Cl_2\,(g) \rightarrow NOCl_2\,(g)$

Molecularity more than three is non existent as the possibility of four particles coming together at the same time is almost nil.

It has been pointed out earlier that the order of a reaction has to be found out from experimental data on the dependence of the rate of the reaction on the concentration of the reactant(s), but its mechanism, including the molecularity of each step, is a matter of speculation. It has also been stated that a reaction takes place in a number of steps. The rate of the overall reaction is often determined by the rate of the slowest step which acts as the '*bottleneck*' for the reaction. *The slowest step in a mechanism is called the* ***rate-determining step.***

For an elementary step of the reaction the rate is proportional to the concentration of each reactant species in the step.

Hence the molecularity of each elementary step of the reaction is the same as the order of that step. A bimolecular step will have second-order kinetics. This, however, does not give the overall order of the reaction.

Let us consider the reaction

$$2NO\,(g) + 2H_2(g) \rightarrow 2H_2O\,(g) + N_2\,(g)$$

Experimentally it is found to be a third-order reaction having the rate law

$$\text{rate} = k\,[NO]^2\,[H_2]$$

It appears that the reaction proceeds by the three-step mechanism

$$\begin{aligned} 2NO\,(g) &\rightarrow N_2O_2\,(g) \\ N_2O_2\,(g) + H_2\,(g) &\rightarrow N_2O\,(g) + H_2O\,(g) \\ N_2O\,(g) + H_2\,(g) &\rightarrow N_2\,(g) + H_2O\,(g) \end{aligned}$$

How the above mechanism came to be proposed can be illustrated by taking a general reaction of the above type, e.g.

$$2A + B \rightarrow C + D$$

Let us say that the experimental rate law for this reaction is

$$\text{rate} = k\,[A]^2\,[B] \tag{12.65}$$

If we assume that the reaction proceeds by a one step mechanism in which two molecules of A and one of B collide together simultaneously, i.e. a *termolecular collision* takes place, then the rate equation would be as shown. However, termolecular collisions being rare one would look for an alternative mechanism which is more realistic. Bimolecular collisions being more common it would be more plausible to see if use of bimolecular elementary steps lead to the experimental rate law.

One possible set of elementary steps would be

$$\begin{aligned} &(1) \quad 2A \rightarrow A_2 \\ &(2) \quad A_2 + B \rightarrow C + D \end{aligned}$$

In this mechanism two molecules of A first combine to form a reaction intermediate A_2 which then reacts with B to form the products C and D. We can see that the sum of the two steps gives the overall reaction. Both of these reactions are unlikely to proceed at the same rate. If it is assumed that step (1) is slow, and once the intermediate is formed it reacts immediately with B to give the products. Elementary reaction (1) is then the rate- determining step (in this case the bimolecular collision between two A molecules) and we can predict that the rate law for this elementary step would be

$$\text{rate} = k\,[A]^2$$

If this is the rate law for the rate- determining step, it will also be the rate law for the overall reaction. However, this cannot be the correct one, because the experimental rate law is different. This does not necessarily mean that this mechanism is wrong, but it does mean that the first step is not the rate-determining step. Let us assume that step (2) is the rate- determining step. The rate equation for this step is

$$\text{rate} = k\,[A_2]\,[B] \tag{12.66}$$

This rate law, however, contains the proposed reaction intermediate (A_2), but the experimental rate law contains only the concentrations of A and B. As we will see the concentration of A_2 can be expressed in terms of the concentrations of A and B.

Once A_2 is formed it can react either of two ways. Since A_2 is proposed to be unstable (if it were stable one could isolate it and there would be no question about the proposed steps) it could undergo decomposition to two molecules of A or collide with a molecule of B to give the products C and D. The mechanism proposed should, therefore, include a reaction that allows A_2 to decompose to two molecules of A.

$$A_2 \rightarrow 2A$$

The total steps in the mechanism would then be

$$\begin{array}{lcll} 2A & \rightarrow & A_2 & \text{(fast)} \\ A_2 & \rightarrow & 2A & \text{(fast)} \\ A_2 + B & \rightarrow & C + D & \text{(slow)} \end{array}$$

If the rate at which the intermediate A_2 is formed from two molecules of A is the same as the rate at which A_2 breaks up to form A molecules, then these two reactions form a state of dynamic equilibrium. Because these reactions are much faster than the third step the equilibrium is reached before any significant reaction by the slower step can take place. The first two equations can then be written in the form

$$2A \rightleftharpoons A_2$$

and the total mechanism, in which the first step is an equilibrium, can be written as below:

$$\begin{array}{lcl} 2A & \rightleftharpoons & A_2 \\ A_2 + B & \rightarrow & C + D \end{array}$$

Since in an equilibrium situation the rate of the forward reaction (rate_f) is equal to the rate of the reverse reaction (rate_r)

$$\text{rate}_f = k_f[A]^2 = \text{rate}_r = k_r[A_2] \quad (12.67)$$

Or simply,

$$k_f[A]^2 = k_r[A_2] \quad (12.68)$$

Solving equation (12.68) for $[A_2]$, we have

$$[A_2] = \frac{k_f[A]^2}{k_r} \quad (12.69)$$

If this value of $[A_2]$ is substituted in equation (12.66) and k_f/k_r is substituted by k the rate expression obtained is

$$\text{rate} = k\,[A]^2\,[B] \quad (12.70)$$

which agrees with the expression derived from experiments.

12.14 Unimolecular Reaction: Lindemann's Mechanism

The collision theory gives a fairly satisfactory account of bimolecular reactions. Difficulty was, however, encountered in explaining the formation of activated complex in the case of some of the reactions that were kinetically of first-order and apparently unimolecular.

The rate of formation of the active molecules by binary collisions should be proportional to n^2, where n is the number of molecules per cm^3. In a bimolecular reaction the rate is also proportional to n^2 and second-order kinetics is followed. In a first-order reaction, however, the rate is proportional to n. In such reactions the rate is not proportional to the rate of formation of active molecules. The question then arises as to how the molecules in such reactions acquire the necessary activation energy.

At one time it was seriously proposed that activation energy is acquired by absorption of radiation from the surroundings, but all attempts to detect such radiation were unsuccessful. The radiation hypothesis has, therefore, been rejected on valid grounds. F. A. Lindemann (1922) showed how activation by collision could lead to first-order kinetics for unimolecular reactions and also explain the breakdown of first-order rate law at low concentrations. He pointed out that molecules could be activated by collisions with other molecules by transfer of energy, and after a molecule has acquired the necessary energy of activation it must remain at that energy state for a while before it can react. If, however, the activated molecule cannot have that 'life time' and undergoes collision, it would be deactivated. This necessarily implies the idea that activated molecules cannot cross over the energy barrier if they enter into other collisions. Consequently, *'activation by collision'* and *'deactivation by collision'* are both possible. The idea can be mathematically treated as follows:

$$\begin{tikzcd} A + A \arrow[r, shift left, "k_1"] & A^* + A \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"] \\ & \text{Products} \end{tikzcd} \quad (12.71)$$

where A^* represents the activated molecule. As one can see (equation (12.71)) the proposed mechanism also considers deactivation of A^*. Now the rate of activation is equal to $k_1\,[A]^2$ and the rate of deactivation is $k_{-1}\,[A^*]\,[A]$. The rate of reaction is, however, $k_2[A^*]$. At steady state

$$\frac{d[A^*]}{dt} = k_1\,[A]^2 - k_{-1}\,[A^*]\,[A[\, - k_2\,[A^*] = 0 \tag{12.72}$$

and, therefore, $$[A^*] = \frac{k_1[A]^2}{k_{-1}[A]+k_2}$$

or $$\text{rate of reaction} = k_2\,[A^*] = \frac{k_1k_2[A]^2}{k_{-1}[A]+k_2} \tag{12.73}$$

Two limiting cases may be considered.

Case 1: At sufficiently high pressure, $k_{-1}[A] >> k_2$, then equation (12.73) may be written as

$$\text{rate} = \frac{k_1k_2[A]^2}{k_{-1}[A]} = \text{const.} \times [A] \tag{12.74}$$

The rate is proportional to the first power of concentration, i.e., the reaction is first-order; that is if the rate of deactivation is sufficiently large, the reaction will follow a first-order rate law. This, of course, means that after activation there is appreciable time lag before the molecules fall apart, and during this time lag the activated molecules may undergo further collisions leading to deactivation.

Case 2: At low pressure $k_2 >> k_{-1}[A]$ then equation (12.73) becomes

$$\text{rate} = k_1\,[A]^2 \tag{12.75}$$

i.e., the reaction becomes kinetically second-order. In this case there is no time lag after activation. The activated complex falls apart immediately after its formation, i.e., the reaction is extremely fast.

It is, therefore, the relative values of k_{-1} and k_2 that really govern the order of a reaction, and not the molecularity. Since the Lindemann's theory emphasises on a *'life time'* for the activated molecule as a necessary condition for reaction, and since the deactivation rate would control the order, a first-order reaction would become a second-order process at extremely low concentration. At very low concentration the average time interval between successive collisions would be large and consequently the probability of deactivation by collision will be small. Search for the breakdown of the first-order process at low pressure for gaseous reactions has met with success. The most widely recognised first-order reaction, viz. the decomposition of N_2O_5, was found to become a second-order process at a pressure below 0.04 mm of mercury. A number of reactions have been found to obey the Lindemann's mechanism.

However, rigorous quantitative treatment of Lindemann's mechanism was found to be inadequate. The mechanism was further modified by Hinshelwood, Rice, Kassel and Slater which will not be considered in this text.

12.15 Theory of Absolute Reaction Rate

Theoretical approach to the calculation of the rates of reaction has been made from a point of view totally different from the collision theory. In the theory of *absolute reaction rate* or the *transition-state theory*, which was developed by Eyring, Glasstone and Laidler, attention is focussed on the activated complex. The activated complex is supposed to be in equilibrium with the reactants. According to absolute rate theory the reaction between A and B may be represented by

$$A+B \rightleftharpoons A\cdots B \rightarrow products$$

where $A\cdots B$ is the activated complex. The equilibrium constant for the formation of the complex is

$$K=\frac{[A\cdots B]}{[A][B]} \tag{12.76}$$

The concentration of the activated complex

$$[A\cdots B]=K[A][B] \tag{12.77}$$

In spite of its ill-defined character the activated complex is regarded as a molecule except that it has one special mode of vibration with respect to which it is unstable. This vibration may be regarded as having a large enough frequency which leads to dissociation of the complex into the products. The rate of the reaction is then the product of the concentration of the activated complex and the frequency of this vibration, ν, i.e.

$$\text{rate} = \nu\,[A\cdots B] \;= \nu\,K\,[A]\,[B] \tag{12.78}$$

But the rate of the reaction $A + B \rightarrow$ Products is

$$\text{rate} = k\,[A]\,[B] \tag{12.79}$$

From equations (12.78) and (12.79) it follows that

$$k = \nu\,K \tag{12.80}$$

From quantum theory it was argued that the frequency of this special mode of vibration is

$$\nu = \mathrm{k}\frac{T}{h} \tag{12.81}$$

where k is the Boltzmann constant and h is the Planck's constant. Equation (12.80) then reduces to

$$k = \mathrm{k}\,\frac{T}{h}\,K \tag{12.82}$$

Since the values of k and h are known, a method of calculation of K would lead to a theoretical calculation of the rate constant. Statistical mechanics provides such a method and the application of its principles reduces equation (12.82) to

$$k = \mathrm{k}\,\frac{T}{h}.\frac{f_{A\cdots B}}{f_A\,f_B}\,e^{-\frac{E_a}{RT}} \tag{12.83}$$

where the f's are known as the partition functions of the species indicated in the subscripts. $f_{A\cdots B}$ does not include the vibration along the reaction co-ordinate. Statistical mechanics enables one to calculate the values of f's from the fundamental physical properties, such as mass, bond distances, vibration frequencies etc. The necessary data, besides mass, are derived from spectroscopic and other measurements. The theory derives its name from this fact. Comparison of equation (12.83) with the Arrhenius equation shows the similarity between the two equations.

Calculation of the values of the partition functions for a reaction between atoms gives a value of $A = k \times \frac{T}{h} . \frac{f_{A\cdots B}}{f_A f_B}$ which is in good agreement with the value of the frequency factor in the collision theory. For reactions between polyatomic molecules it turns out that the consideration of the different degrees of freedom of the molecules leads to a rate constant in which the pre-exponential factor differs from that obtained in the collision theory by a factor $(f_v/f_r)^5$. Here f_v and f_r are the vibrational and rotational partition functions for each such degree of freedom. This quantity, therefore, must be equal to P in equation (12.84), i.e.,

$$P = \left(\frac{f_v}{f_r}\right)^5 \tag{12.84}$$

From the calculated values of f_v and f_r, P turns out to have a value ranging from 10^{-5} to 10^{-6}. For reactions between an atom and a diatomic molecule P comes out to have a value of 10^{-1} to 10^{-2}. As pointed out in *Section 12.10* the experimental values of P for many reactions fall within this range.

In conclusion it must, however, be said that none of the theories has yet reached a stage which might be stated as completely satisfactory. It must not be construed that attempts are lacking, but the fact is that the question of the mechanism of reactions is rather complex, even in the case of such apparently simple reaction as the formation of water from hydrogen and oxygen.

CHAIN REACTIONS

One type of complex reaction is the chain reaction. These reactions take place by way of a very reactive intermediate such as a free atom or a free radical - a group of atoms or an ion containing an unpaired electron. These reactive intermediates could be prepared by heating some molecules at a high temperature or by absorption of light of suitable wavelength. Once created they can react with other molecules to form a product *plus* yet another free atom or a free radical. This process, once initiated, can be repeated over and over again, making the reaction *self-propagating*. In chain reactions many molecules react for every free atom or free radical formed. As a result the rate of the reaction rapidly increases unless the self-propagating steps are terminated by some mechanism.

12.16. Hydrogen-Chlorine Reaction

An example of chain reaction is the reaction between hydrogen and chlorine gas in the presence of light. According to the laws of photochemistry (*Section 12.22*) one quantum of radiation is absorbed by one molecule of the reactant producing two atoms of chlorine. In the case of hydrogen-chlorine reaction it was found that as many as 106 molecules of HCl are produced for each quantum of radiation absorbed. Such a large yield of HCl as a result of the break up of only one molecule of chlorine was explained using the following steps:

1. $Cl_2 + light \rightarrow Cl\bullet + Cl\bullet$
2. $Cl\bullet + H_2 \rightarrow HCl + H\bullet$
3. $H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$
4. $Cl\bullet + H_2 \rightarrow HCl + H\bullet$ etc.

The first step in the reaction is the absorption of radiation by chlorine molecules resulting in the production of two chlorine atoms, which are very reactive. In step 2 is shown the reaction between a chlorine atom and a hydrogen molecule when a hydrogen atom is produced. This, in turn, reacts with a molecule of chlorine to produce one molecule of hydrogen chloride and one atom of chlorine. This chlorine atom reacts again and the cycle is repeated. A reaction which was started with the formation of two chlorine atoms has now become self-propagating and a chain reaction takes place. It would seem from this discussion that the reaction will continue to proceed in this manner till all the reactants are consumed. Such, however, is not the case as one or more of the following reactions,

5. $Cl\bullet + Cl\bullet \rightarrow Cl_2$
6. $H\bullet + H\bullet \rightarrow H_2$
7. $H\bullet + Cl\bullet \rightarrow HCl$

may terminate the self-propagating steps of the chain. Such reactions are usually known to occur in the presence of a third body, usually the wall of the container, which can take away the energy liberated when the atoms combine. Step 1 is known as the *initiation step* as the chain starts as a results of this reaction. Steps 2 to 4 are the *chain propagating steps* while steps 5 to 7 are the *terminating steps*, as the chain of production of chlorine atom is blocked by these reactions.

The essential features of chain reactions are that there are three distinct steps in the reaction:

(a) Initiation, (b) Propagation and (c) Termination

Chain reactions may also be brought about by free radicals, such as $CH_3\bullet$, $C_2H_5\bullet$ etc. The free radicals play an important role in the synthesis of high polymers. The free radicals may be produced thermally or photochemically. The existence of free radicals, such as $CH_3\bullet$, $C_2H_5\bullet$, $OH\bullet$ etc. which violate the ordinary rules of valence theories, has been established by spectroscopic and chemical means.

12.17 Branching Chains: Explosive Reactions

There are many chemical reactions which proceed so swiftly that the reactions are completed within a fraction of a second. These reactions result in explosions. A familiar example is the explosive reaction when the mouth of a test tube filled with hydrogen gas is held near a flame. Hydrogen and oxygen of air combine to form water which condenses. Such explosions are believed to take place as a result of *chain branching*.

Another type of explosions, known as *thermal explosions*, take place if a highly exothermic reaction is carried out in a confined space from which heat cannot be dissipated. The heat evolved during the reaction increases the temperature, thereby increasing the rate of the reaction very rapidly and ultimately causing an explosion.

In an ordinary chain reaction each propagating step leads to the formation of a molecule of product and a chain carrier. If more than one chain carrier is produced from the original active species then the chain is said to branch. Each new carrier now can propagate its own chain so that the number of chain carriers multiplies rapidly.

12.18 Hydrogen-Oxygen Reaction

The gas phase reaction between hydrogen and oxygen to produce water is quite complex. Experimentally it is found that the reaction rate is dependent on pressure. A mixture of H_2 and O_2 in the ratio 2:1 reacts slowly in the temperature range of 450°- 600°C as long as the pressure is very low. At a temperature of 550°C if the pressure exceeds about 2 mm Hg the mixture explodes. If, however, the reaction is started at an initial pressure of about 200 mm Hg the reaction is steady and proceeds at a measurable speed. On decreasing the pressure the rate decreases but below about 100 mm Hg pressure the reaction is again explosive. Thus at this temperature there is a region of pressure within which there is explosion, but above and below which the reaction rate is steady. This is shown schematically in Figure 12.22.

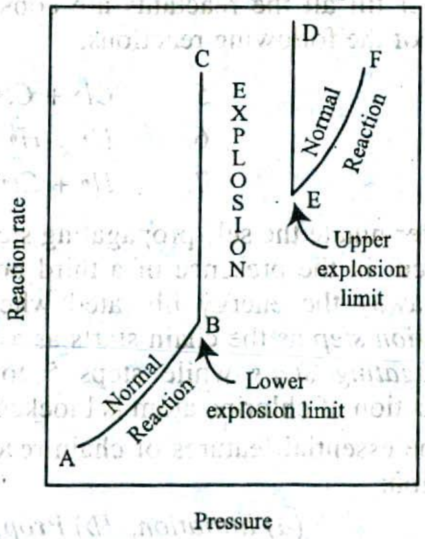


Figure 12.22 Explosion limits (third explosion limit not shown).

The proposed mechanism for the hydrogen-oxygen reaction is considered to have the following steps :

(1) $H_2 \rightarrow 2H\bullet$ Intitiation

$$\begin{array}{ll}
\left.\begin{array}{l}
(2)\ H\bullet + O_2 \rightarrow \bullet OH + O\bullet \\
(3)\ O\bullet + H_2 \rightarrow \bullet OH + H\bullet
\end{array}\right\} & \text{Branching} \\
(4)\ \bullet OH + H_2 \rightarrow H_2O + H\bullet & \text{Propagation} \\
\left.\begin{array}{l}
(5)\ H\bullet + Wall \rightarrow \text{removal} \\
(6)\ \bullet OH + Wall \rightarrow \text{removal} \\
(7)\ \bullet O + Wall \rightarrow \text{removal}
\end{array}\right\} & \text{Termination}
\end{array}$$

Chain branching occurs in steps (2) and (3) and the reactions (5), (6) and (7) are the chain termination steps. The chain is propagated by step (4)..

Other well-known examples of chain reactions are the nuclear fissions which when allowed to proceed uninhibited gives rise to explosions. The explosion of atomic bomb is of this type.

PHOTOCHEMISTRY

The branch of chemistry which deals with chemical reactions mediated by *light* is called photochemistry. The term '*light*' is used to include all kinds of radiation. In practice, however, photochemical studies are confined to the visible and ultraviolet part of the electromagnetic spectrum. The wavelength range of interest is from 180 *nm* to 700 *nm*. Infra-red radiation (wavelength> 700 *nm*) is too weak to bring about a chemical reaction. X-ray (wavelength ≈ 10 *nm*) produces ionization of molecules and its effect is now-a-days included in the science of radiation chemistry.

In dealing with photochemical reactions light may be regarded as small packets of energy or quanta of energy, called the *photon*, The energy, $\in$, of the photon is, given by quantum mechanics as

$$\in = h\,\nu = h\left(\frac{c}{\lambda}\right) \tag{12.85}$$

where ν is the frequency (= c/λ) of the radiation, h is the Planck's constant ($h = 6.626 \times 10^{-34}$ Js), c is the velocity of light and λ is the wavelength of radiation. The energy of Avogadro number of light quanta is called an *Einstein*. The energy corresponding to radiation of a particular wavelength may easily be calculated.

$$E = N\in = N\,h\,\nu = N\,h\,(c/\lambda) \tag{12.86}$$

If we substitute the values of N (6.022×10^{23} mol^{-1}), h (6.626×10^{-34} Js) and c (3.0×10^{8} ms^{-1})in equation (12.86) we get,

$$E = \frac{(6.022\times10^{23})(6.626\times10^{-34})(3.0\times10^{8})}{\lambda}$$

$$E = \frac{0.1197}{\lambda}\ J\,mol^{-1} = \frac{11.97\times10^{-5}}{\lambda}\ kJ\,mol^{-1} \tag{12.86a}$$

Here λ is in meter.

Example12.9: Calculate the value of Einstein of energy for radiation of wavelength 400 *nm*.

Solution: 400 $nm = 4 \times 10^{-5}\ cm = 4 \times 10^{-7}\ m$

$$\text{Or } E = \frac{11.97\times10^{-5}}{4\times10^{-7}} = 299.25\ kJ\ mol^{-1}$$

Example12.10: Calculate the wave length of light in meter if the energy of radiation is 500 *kJ mol⁻¹*.

Solution: Substituting in equation (12.86) we get,

$$E = \frac{11.97\times10^{-5}}{\lambda}$$

or

$$\lambda = \frac{11.97\times10^{-5}}{500} = 2.94 \times 10^{-7}\ m$$

Note: λ is generally expressed in Å. We know 1 Å $= 10^{-8}\ cm = 10^{-10}\ m$

In Table 12.8 a few such values along with the effect of the various radiations are collected.

Table 12.8 Wavelength of radiation related to frequency, energy, nature of effect etc.

Wavlength *nm* ($10^{-9} m$)	Frequency cm^{-1}	Nature of radiation	Energy, einstein $kJ\ mol^{-1}$	Nature of effect produced
1,00,000	3×10^{12}	Far infra-red	1.20	Kinetics & rotational
10,000	3×10^{13}	Infra-red	12.0	Rotational and vibrational
700	4.3×10^{14}	Red	171	Electronic transition, more so from blue to downwards
600	5.0×10^{14}	Yellow	199	
500	6.0×10^{14}	Blue	238	
400	7.5×10^{14}	Edge of violet	297	
300 – 100	$(1\text{-}3) \times 10^{15}$	Ultraviolet	398 – 1195	Electronic transition much more than in the visible region
0.1	10^{18}	X-rays	12.0×10^{5}	High energy Electronic and nuclear transition
0.01-0.001	$10^{19} - 10^{20}$	γ-rays	12.0×10^{6} 12.0×10^{7}	Manyfold, complex

12.19 Absorption of Light: Beer-Lambert Law

If material bodies are exposed to radiation, part of the incident radiation is absorbed, a part is scattered and a part is transmitted. As a result of absorption the intensity of light passing through material bodies, i.e. the intensity of transmitted light, decreases. The fraction of incident light absorbed depends on the thickness of the absorbing medium. Lambert derived a quantitative relationship between the decrease in intensity of a monochromatic light due to the passage through a homogeneous medium of thickness dx and the intensity of light I. This law is known as Lambert's law, and may be stated as

> *The decrease in intensity of light with thickness of the absorbing medium at any point is directly proportional to the intensity of light.*

Mathematically it can be expressed as,

$$-\frac{dI}{dx} \propto I \tag{12.87}$$

where dI is a small decrease in intensity of light upon passing through a small distance dx and I is the intensity of the monochromatic light just before entering the medium. Equation (12.87) may be written as

$$-\frac{dI}{dx} = aI \tag{12.88}$$

where $-\frac{dI}{dx}$ is the rate of decrease of intensity with thickness dx, a is called the *absorption co-efficient*. Integration of equation (12.88) after rearrangement gives,

$$-\ln I = ax + C \tag{12.89}$$

where C is a constant of integration. At $x = 0, I = I_0$. So, $C = -\ln I_0$. Introducing this in equation (12.89) we get,

$$\ln \frac{I}{I_0} = -ax \tag{12.90}$$

Equation (12.90) can also be written as,

$$I = I_0 e^{-ax} \tag{12.91}$$

Equation (12.90) can also be written as,

$$\log \frac{I}{I_0} = -\frac{a}{2.303} x \tag{12.92}$$

or,

$$\log \frac{I}{I_0} = -a'x \tag{12.93}$$

where $a' \left(= \frac{a}{2.303}\right)$ is called *extinction co-efficient* and $-\ln \frac{I}{I_0}$ is termed *absorbance* of the medium. Absorbance is represented by A.

Lambert's law was extended by Beer who showed that when light passes through a solution of a given thickness the fraction of incident light absorbed is dependent not only on the intensity I of light but also on the concentration c of the solution. This is known as the Beer's law. The two laws may be combined to write

$$-\frac{dI}{dx} \propto I \times c$$

or,
$$-\frac{dI}{dx} = b \times I \times c \tag{12.94}$$

When the concentration, c, is expressed in $mol\ L^{-1}$, b is called the *molar absorption co-efficient.* As in the case of Lambert's law equation (12.94) may be transformed into,

$$log \frac{I}{I_0} = -\frac{b}{2.303} \times c \times x$$

(12.95)

or,
$$log \frac{I}{I_0} = -\in c\ x \tag{12.96}$$

where $\in\ (= \frac{b}{2.303})$ is called the *molar extinction co-efficient* which is expressed in $L\ mol^{-1}\ cm^{-1}$. The expression (equation 12.96) is commonly known as Beer-Lambert's law.

The *molar extinction co-efficient* $\in$ is dependent on the nature of the absorbing solute as well as on the wave length of the incident light used. Equation (12.96) is the basis of all colorimetric and spectro-photometric measurements. These laws are, however, obeyed strictly by monochromatic radiation and solutions of low concentration.

12.20 Consequences of the Absorption of Light

Light is a form of energy. Absorption of light means absorption of radiation energy. Absorption of radiation energy by a substance may lead to the following changes:

(i) *Thermal change*: The kinetic energy of the molecules may be increased giving rise to an increase of temperature, i.e., heat will be generated.

(ii) *Excitation*: The internal energy of the molecules or atoms may be raised. This will result in elevating the electrons to higher energy levels. In spectroscopic terminology it is assumed that the atoms or molecules are raised from the ground state energy levels to the excited state energy levels.

(iii) *Dissociation*: The molecule breaks down to form smaller molecules, atoms or free radicals. Excitation and dissociation may occur simultaneously.

(iv)*Emission*: Part of the absorbed radiation may be re-emitted giving rise to *fluorescence or phosphorescence (Section 12.21).*

The first of the four processes is not important when visible and ultraviolet light are considered. The other three processes will be of interest in discussing the phenomenon presented in *Section 12.21.* When light of shorter wavelengths is used, in addition to the above processes ionization and physical interaction of the photons and matter become also prominent.

12.21 Luminescence

As a result of the absorption of light, molecules or atoms are excited, i.e. have more energy. In nearly all cases some or all of the extra energy is dissipated as heat. When the substance does not undergo photo-chemical reaction, however, some of the energy is re-emitted as radiation. The substance is then said to show ***luminescence***. The emission of light in the visible region of the spectrum is attributed to the return of one or more of the outer electrons of the excited molecules or atoms to the normal position as a result of collisions with other atoms or molecules. De-activation of the excited molecules may also occur by chemical, electrical or other forms of interaction.

Fluorescence: Emission of light by excited atoms or molecules soon after excitation has stopped is known as fluorescence. In fluorescence the life time of the excited molecules or atoms is of the order of 10^{-6} seconds or lower, i.e., the emission takes place within 10^{-6} seconds or less after irradiation. Fluorescence practically ceases when the incident irradiation has stopped. The wavelength of the emitted radiation is, in general, greater than that of the incident radiation. This indicates that some energy is left in the absorbing molecules. This fact was discovered by Stokes. There are a number of exceptions to this law.

Numerous substances exhibit fluorescence. Examples are uranium, glass, petroleum, solution of quinine sulphate, vapours of sodium, mercury, iodine etc. Fluorescein and eosin are common examples of fluorescent substances.

Phosphorescence: If the emission of light continues after the source of exciting radiation is cut off the phenomenon is known as phosphorescence. The period of phosphorescent radiation may be a few seconds or more. Sulphides of alkaline earth metals are good examples of phosphorescent substances.

Both phosphorescence and fluorescence are affected by the presence of a third body in the system. These bodies absorb some energy by way of collisional transfer from the excited molecules and reduce, or even stops, phosphorescence and fluorescence. These substances are known as quenching agents. If the process of de-excitation of the excited molecules is delayed by some means, the substance shows phosphorescence instead of fluorescence. Thus a solution of fluorescein in glycerol exhibits phosphorescence. The viscous nature of the glycerol solution reduces the collision frequency and the energy cannot be dissipated as easily. This is why phosphorescence is mainly found in solids.

Luminescent materials have wide use in our every-day appliances. The so-called radium dials of watches and clocks, in fact, contain a long-life phosphroescent material made by mixing zinc sulphide and a radioactive material with a binder. These materials absorb radiation during daytime or from the lamp and then glows in the dark. Phosphorescent paints have been developed. These are extensively used in roads and highways to indicate sharp turns, bends etc. Edges of furniture, tips of electric switches etc. are impregnated with phosphorescent materials to make them visible in the dark.

Chemiluminescence: is the phenomenon of emission of light as a result of certain chemical reactions. The slow oxidation of white phosphorus is an example. Other examples of chemiluminescence are the oxidation of decaying wood containing certain forms of bacteria, fire-flies etc. The oxidation of 3-aminophthalic cyclic hydrazide, commercially known as luminol, by hydrogen peroxide in alkaline medium is accompanied by a bright green luminescence.

Radiation of short wavelengths, such as x-rays or γ-rays, produces luminescence in solids. When x-rays are passed through sodium chloride the crystals become yellow and potassium chloride shows blue colour. Such phenomena are considerably more complicated than simple luminescence.

12.22 The Laws of Photochemistry

There are two basic laws of photochemistry. In 1817 Grotthus and later Draper stated that *only that radiation which is absorbed by a substance is effective in producing a photochemical reaction.* This is known as the Grotthus-Draper law. It does not follow, however, that all the light that is absorbed will produce a reaction. The various possible effects were pointed out in *Section 12.21.*

A significant advance was made by Einstein and later by Stark who applied the concept of the quantum of energy to photochemical reactions of molecules. They formulated a law, known as the *law of photochemical equivalence*, which states that *each molecule taking part in a reaction induced by exposure to radiant energy absorbs one quantum of radiation causing the reaction.* It should be emphasized that this applies only to the primary process of light absorption. A molecule on absorption of energy does not necessarily undergo reaction; again one activated molecule may cause the reaction of a large number of molecules through a chain mechanism. Hence the law should not be taken as to mean that one molecule reacts for each quantum absorbed. The ratio of the number of molecules reacted to the number of quanta of radiation absorbed is called the *quantum efficiency* or *quantum yield* (Φ), i.e.,

$$\Phi = \frac{\textit{Number of molecules reacted}}{\textit{Number of quanta absorbed}} \tag{12.98}$$

This then is the relation between the amount which undergoes photochemical reaction and the amount of radiant energy absorbed. In an idealized system the quantum yield should be unity. For several reactions, $\Phi = 1$; for many reactions $\Phi > 1$, while for others $\Phi < 1$.

As a matter of fact deviations from the law of photochemical equivalence are considered to be due to one or more side-effects and explanations for these have been offered. In some cases a quantum yield of 2 is in accordance with the Einstein-Stark law. For example, the photochemical reaction between hydrogen and iodine takes place according to the following scheme:

$$\begin{aligned} I_2 &\xrightarrow{hv} I\bullet + I\bullet \\ I\bullet + H_2 &\rightarrow HI + H\bullet \\ H\bullet + I\bullet &\rightarrow HI \end{aligned}$$

Each quantum of absorbed radiation forms two hydrogen iodide molecules, yielding a Φ value of 2. However, in the reaction between hydrogen and chlorine Φ is very large and may assume a value of 10^6. Such high values of Φ definitely indicate chain mechanism in the reaction. Several reactions are also known where Φ assumes values much lower than unity. These low values are mainly due to fluorescence, phosphorescence and other side-effects. When a solution of anthracene in benzene is exposed to ultraviolet radiation, two molecules of anthracene combine to form dianthracene, $2C_{14}H_{10} \rightarrow C_{28}H_{20}$. The reaction is accompanied by fluorescence and the quantum yield is low in dilute solution due to de-excitation. When the concentration of anthracene is increased in the solution the quantum yield increases whereas fluorescence decreases. At sufficiently high concentration the quantum yield assumes a limiting constant value and fluorescence practically disappears.

In photochemical decomposition of ammonia the quantum yield varies from about 0.1 to 0.5 depending on the temperature of the reaction. The low quantum yield in this reaction is not due to fluorescence but due to side reactions. The final products of the photolysis are hydrogen, nitrogen and hydrazine. The mechanism of the reaction is suggested to be as follows:

$$\begin{aligned} NH_3 &\xrightarrow{h\nu} \bullet NH_2 + H\bullet \\ \bullet NH_2 + \bullet NH_2 &\rightarrow N_2 + 2H_2 \\ \bullet NH_2 + \bullet NH_2 &\rightarrow N_2H_4 \\ H\bullet + H\bullet &\rightarrow H_2 \end{aligned}$$

The fact that excited molecules in many cases, particularly in gaseous systems, cannot fluoresce due to loss of energy by collision is evident from the behaviour of NO_2 when excited by a radiation of about 400 *nm*. At atmospheric pressure fluorescence is very little but as the pressure is reduced fluorescence increases and becomes quite appreciable at pressures below 1 mm of Hg. The behaviour is schematically shown in Figure 12.23.

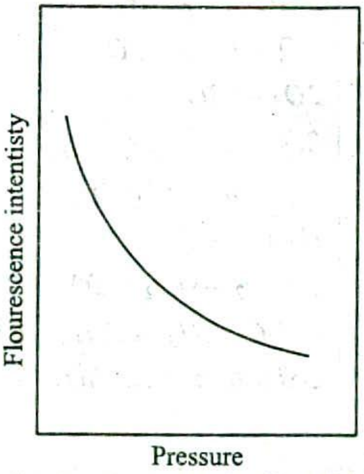


Figure 12.23 Fluorescence intensity of excited NO_2 plotted against pressure.

The photolysis of acetone vapour produces mainly C_2H_6 and CO according to the equation

$$CH_3COCH_3 \xrightarrow{h\nu} C_2H_6 + CO$$

but the mechanism is not represented by this equation. A detailed study has shown the presence of methane, biacetyl and $CH_3\bullet$ radicals in the reaction. The accepted mechanism is

$$\begin{array}{lcl}
CH_3COCH_3 & \xrightarrow{hv} & CH_3\bullet + CH_3CO\bullet \\
CH_3\bullet + CH_3\bullet & \rightarrow & C_2H_6 \\
CH_3CO\bullet + CH_3CO\bullet & \rightarrow & (CH_3CO)_2 \\
CH_3CO\bullet & \rightarrow & CH_3\bullet + CO \\
CH_3\bullet + CH_3CO\bullet & \rightarrow & (CH_3)_2CO
\end{array}$$

The quantum yield is about 0·17, a very low value. The value is thought to be due to the recombination shown in the last step. Some typical photochemical reactions are given in Table 12.9.

Table 12.9 Some photochemical reactions

Reaction	Quantum yield	Remarks
$2HI \rightarrow H_2 + I_2$	2	
$2HBr \rightarrow H_2 + Br_2$	2	
$H_2 + Cl_2 \rightarrow 2\,HCl$	$10^4 - 10^6$	Chain reaction
$3O_2 \rightarrow 2O_3$	3	
$2\,NOCl \rightarrow 2NO + Cl_2$	2.1	
$CO + Cl_2 \rightarrow COCl_2$	10^3	Chain reaction
$2O_3 \rightarrow 3O_2$	2	
$SO_2 + Cl_2 \rightarrow SO_2Cl_2$	1	
$H_2 + Br_2 \rightarrow 2HBr$	$\approx 0{\cdot}01$	Complex
$H_2 + I_2 \rightarrow 2HI$	2	
$2\,ClO_2 \rightarrow Cl_2 + 2O_2$	2	
$CH_3COCH_3 \rightarrow C_2H_6 + CO$	0.17	Complex
Oxidation of Na_2SO_3	5×10^4	Complex chain reaction

12.23 Determination of Quantum Yield

For experimental determination of Φ, the number of molecules reacting per unit time and the quanta of radiation absorbed per unit time must be known. The first quantity can be measured by a number of ways.

If a gaseous reaction involves a change in volume, manometric methods are most convenient; for reaction of other types either the reactant or the product can be analysed by physical methods.

The second quantity, i.e., the number of quanta absorbed is determined by measuring the intensity of the monochromatic radiation before and after passing through the system. The intensity can be measured by a thermopile or bolometer. Photoelectric cells also can be used to measure the intensity of radiation. They are most suitable for comparative study. If, however, one or two suitable reactions can be found out whose quantum yields and rates of reaction are accurately known, these reactions can be used to measure the intensity of radiation. Devices which use such reactions are known as ***actinometers*** which are frequently used. Since the rates of reaction vary with the wavelength, these reactions must be standardized for different wavelengths. The reduction of $HgCl_2$ by $(NH_4)_2C_2O_4$, in presence of trace quantity of ferric salt, to Hg_2Cl_2 can be used for measurement of intensity of radiation. The reaction concerned is

$$HgCl_2 + (NH_4)_2C_2O_4 \rightarrow 2NH_4Cl + CO_2 + Hg_2Cl_2$$

The extent of reaction can be easily measured by weighing the amount of Hg_2Cl_2 formed. Another reaction commonly used is the decomposition of oxalic acid to carbon dioxide by radiation in presence of uranium salt which acts as a sensitizer. The unreacted oxalic acid is determined by titrating with potassium permanganate after exposure to the radiation for a definite time. From these data the rate of the absorption of radiation quanta is calculated.

12.24 Photosensitized Reaction

There are many substances which do not normally react when exposed to light. If, however, another substance is added to it, photochemical reaction readily proceeds. The substance thus added does not undergo any chemical change. It merely absorbs light energy and then passes it on to the reactant substance. The added substance is called a *photosensitizer*, since it sensitizes the reaction. The process is termed as *photosensitization*. The photosensitizer acts as a carrier of energy from the excited molecule to the reactant molecule.

If only hydrogen gas is irradiated by ultraviolet light of $\lambda = 253.70\ nm$ the molecules do not dissociate to the atoms. But if the same radiation acts on hydrogen in presence of *Hg*-vapour, the hydrogen molecules undergo dissociation to the hydrogen atoms.

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow Hg + 2H$$

The radiation excites the mercury atoms, and the excited mercury atoms transfer the energy to the hydrogen molecules by collision. The reactions occur as a result of transference of energy from photochemically excited molecules by collision- in this case from *Hg* to H_2 molecules.

Another photosensitized reaction is the decomposition of oxalic acid in presence of uranyl sulphate.

$$UO_2^{2+} + h\nu \rightarrow UO_2^{2+*}$$

$$UO_2^{2+*} + (COOH)_2 \rightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The uranyl ion acts as a photosensitizer.

The decomposition of ozone in ordinary light by a trace of chlorine is an example of photosensitized reaction. In ordinary photographic films or plates silver bromide is the active ingredient which is decomposed by visible light of the shorter wavelength region. Thus red and orange bodies appear equally dark in the print. However, if suitable photosensitizers are mixed with the silver bromide the latter becomes sensitive to the entire part of the visible spectrum. Such films are known as panchromatic films. These give a more natural and livelier picture than the orthochromatic films.

12.25 Photosynthesis

Some very important reactions take place in nature by the action of light. One such reaction is the synthesis of macromolecules in the plant kingdom and is known as *photosynthesis*. The formation of carbohydrates by plants in presence of light from CO_2 and H_2O with the help of *chlorophyll* as sensitizer is an example of natural photosynthesis. The detailed mechanism has so far been elusive. Several man-made high polymers are now synthesized by photochemical processes and photochemistry is now an important branch for kinetic studies.

12.26 Radiation Chemistry

Chemical reactions brought about by the action of α, β, γ and X-*rays*, by rapidly moving electrons and by high voltage discharges are included in Radiation Chemistry. As the energies of such radiation are very large the absorption of these radiations is accompanied by ejection of electron from the atoms of absorbing materials. This will cause ionization. The secondary electrons thus released have high kinetic energy and may cause excitation, dissociation or further ionization. The processes are complicated.

KINETICS OF HETEROGENEOUS REACTIONS

It has been mentioned earlier that many reactions are greatly influenced by the walls of the containing vessel or by the presence of a solid surface, such as metals, metal oxides and salts. These material bodies, by virtue of their presence, not only accelerate or retard a reaction but often alter the very nature of the reaction. Primary alcohols on decomposition may give either olefines and water or aldehydes and water depending on the nature of the solid. This class of reactions which are influenced or modified due to the presence of material body constituting a different phase is termed ***heterogeneous reactions***. The effect of solid phase, which will be designated henceforth as third body, is quite specific in nature. Instead of trying to go deep into the subject, attempts will be made to study the effect of pressure and temperature only. Further discussions will be made in connection with heterogeneous catalysis (*Section 13.2.2*) and adsorption (*Section 18.3*)

12.27 Gas – Solid Systems: Reactions Involving One Gas

The following derivation, based on Langmuir's theory of unimolecular adsorption layer (*Section 18.4*), is made on the assumptions that

(i) the solid surface has a fixed number of adsorption sites,
(ii) the properties of all adsorption sites are the same,
(iii) each site can hold only one adsorbed molecule,
(iv) the heat of adsorption is independent of the adsorption sites.

Let us consider one cm^2 area of a solid surface. Let θ be the fraction covered as a result of adsorption so that the remaining $(1-\theta)$ is bare. Since the number of molecules striking the surface is proportional to the gas pressure P, then $Pk_1(1-\theta)$ gives the rate of adsorption. The number of molecules leaving the surface per unit time, i.e. the rate of desorption, is given by $k_2\theta$. At equilibrium

$$Pk_1(1-\theta) = k_2\theta \tag{12.99}$$

Rearrangement of equation (12.99) gives

$$\theta = \frac{k_1P}{k_2 + k_1P} \tag{12.100}$$

k_1 and k_2 being two constants. This relation gives rise to three important situations::

(a) *Surface nearly bare,* i.e., little adsorption: Since θ in this case is very small we can write $k_1P(1-\theta) = k_1P$ since $(1-\theta) \approx 1$

so that $$k_1P = k_2\theta$$

or $$\theta = \frac{k_1}{k_2}P \tag{12.101}$$

which shows that $\theta \propto P$. In such cases the reaction rate will be proportional to the first power of the gas pressure and, therefore, kinetically first-order, i.e., rate = kP. The decompositions of PH_3 on glass, N_2O on gold, HI on platinum and AsH_3 on glass are some examples of first-order heterogeneous gas reactions.

(b) *Surface nearly covered*: $\theta \approx 1$. In such cases

$$k_1P(1-\theta) = k_2$$

or $$(1-\theta) = \frac{k_2}{k_1}\frac{1}{P} \tag{12.102}$$

which shows that when adsorption is almost complete the extent of free surface is inversely proportional to pressure P. However, with further adsorpion the rate of the reaction becomes independent of pressure, i.e., $rate = kP^o = k$. This happens because there is no space on the surface where adsorption can take place. Thus the reaction becomes kinetically zero-order. Decomposition of HI on gold surface, and NH_3 on tungsten, are examples of zero-order reactions.

(d) *Intermediate case*: In this case the general rate can be expressed as:

$$\text{rate} = kP^n \quad \text{where } 1 > n > 0.$$

The decomposition of SbH_3 on glass is an example where $n = 0{\cdot}6$. These are reactions of fractional orders.

On the basis of the above reasoning for the three cases it can be readily shown that when the surface is nearly bare the rate of reaction,

$$\frac{-dP}{dt} = k_1P \tag{12.103}$$

where k_1 now stands for the velocity constant since pressure of gas is a measure of its concentration. The reaction is, therefore, a first-order one. When, however, the surface is nearly covered the rate of the reaction becomes equal to $k_1P^o = k$, i. e., proportional to the zero power of concentration. The reaction, therefore, becomes kinetically zero- order.

(d) Autocatalysis: In the foregoing discussions the question of adsorption of the products on the surface has not been considered. However, this occurs often and since the surface gets covered the reaction is modified. The decomposition of SbH_3 is a slow reaction on glass but the reaction is greatly accelerated by Sb itself. Consequently, the Sb formed as a result of the reaction accelerates the rate since Sb remains adsorbed on the glass surface. This is a case where the product of the reaction itself acts as a catalyst. Such reactions are called *autocatalytic reactions* and the phenomenon is known as *autocataysis*. The reverse phenomenon is, however, more common. The product of the reaction often covers a considerable portion of the surface and thereby retards the rate of the reaction. When ammonia is thermally decomposed on platinum surface and the hydrogen formed as a result of the reaction, $2NH_3 \rightarrow N_2 + 3H_2$, is strongly adsorbed and covers the free platinum surface the reaction is slowed down. SO_3, formed in the contact process, exerts a similar retardation effect where platinum is the catalyst. The rate is found to be inversely proportional to 0.5 power of the SO_3 concentration. The surface is said to be poisoned and the phenomenon is known as *autoretardation*. External gases, small solid particles carried over by a reacting gas etc. quite often poison the catalysts in many reactions and extreme care is needed to free the reaction gas from such poisons. Water vapour acts as a poison in NH_3 synthesis by Haber's process. Dust particles, arsenic compounds are strong poisons for platinum in the contact process for H_2SO_4 manufacture. NO acts as strong inhibitor for many reactions in gas phase where free radical mechanism is involved. The kinetics of autocatalytic and *autoretarded* reactions are quite complicated and often insolvable. In a number of reactions the concentration of the poison or the catalyst enters into the rate expression.

12.28 Gas-Solid Systems: Reactions Involving Several Gases

When more than one reacting gases are involved in a chemical reaction, the overall rate will depend on the relative extent of adsorption of the different gases. If one of the gases is more strongly adsorbed and covers a large fraction of the surface with an adhering film the rate would be mainly governed by the adsorption of the other constituent on the bare part of the surface. In the combination of ethylene and hydrogen on copper surface around 0°C, ethylene is strongly retained on the surface leaving a small free surface and thus retards the reaction. The rate would be controlled by the adsorption of hydrogen on the bare surface. Thus although the reaction is bimolecular, kinetically it would behave like a first order one. The rate expression assumes the form

$$\text{rate} = k\frac{[H_2]}{[C_2H_4]} \tag{12.104}$$

Such cases are analogous to auto-retardation. The same reaction when studied at 200°C appears to be kinetically second order. On raising the temperature the surface becomes nearly bare and the rate is governed by the adsorption of both the reactants in close proximity. At high temperature the rate equation has been found experimentally to be

$$\text{rate} = k\,[H_2]\,[C_2H_4] \tag{12.105}$$

It is thus apparent that both adsorption and desorption are important and the rate expressions of heterogeneous reactions are really controlled by both adsorption and desorption.

12.29 Heterogeneous Reactions in Solution

Heterogeneous reactions are also known in solutions. The decomposition of H_2O_2 is greatly accelerated by dust, glass, wool, rough surface, gold, platinum etc. The acceleration of decomposition by metals and metal oxides are thought to be due to formation of unstable oxides on the surface which, in turn, decomposes giving off oxygen and thus regenerates the metal or the oxide:

$$H_2O_2 + M \rightarrow MO \text{ or } MO_2 + H_2O$$
$$MO \text{ or } MO_2 \rightarrow M + O_2$$

where *M* stands for the metal or its oxide. The action of dust, glass etc. cannot be accounted for by this mechanism.

QUESTIONS AND PROBLEMS

1. Write a short definition of each of the following terms: (a) rate of a reaction; (b) order of a reaction; (c) rate constant or specific rate constant; (d) initial rate; (e) half-life.
2. At about 190°C methyl isocyanide ($CH_3{-}N{\equiv}C$) in the gas phase is converted to methyl cyanide ($CH_3{-}C{\equiv}N$). For the determination of the kinetics of the reaction the pressure of ($CH_3{-}N{\equiv}C$) as a function of time was determined. The following data were obtained:

Time(sec)	0	1000	2000	5000	10,000	15,000	20,000	30,000
Pressure (mm Hg)	150	142	135	115	88.8	68.2	52.4	31.0

Taking pressure as a measure of concentration draw a graph of pressure *vs* time, calculate two half-lives from the graph and show that the reaction is first order.

3. In a series of experiments for the reaction of NO with Br_2 at 273°C

$$2NO\,(g) + Br_2\,(g) \rightarrow 2NOBr\,(g)$$

the following data were obtained.

Experiment	Initial concentration (mol L^{-1})		Initial rate (mol L^{-1} s^{-1})
	NO	Br_2	
1	0.10	0.10	12
2	0.10	0.20	24
3	0.10	0.30	36
4	0.20	0.10	48
5	0.30	0.10	108

Determine the rate law for the reaction and compute the value of the rate constant.

4. Distinguish between 'order' and 'molecularity' of a reaction. Under what circumstances 'order' and 'molecularity' can become identical?
5. The optical rotation of sucrose in 0.9 mol L^{-1} HCl at various times is given in the following table:

Time (in minutes)	0	10	20	30	40	80
Rotation (in degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	−14.1

Calculate the order of the reaction.

6. Use the following data to show that the decomposition of H_2O_2 in aqueous solution is a first order reaction:

Time (in minute)	0	15	30
N	25.4	9.83	3.81

where N is the volume in mL of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution.

7. In a certain first order reaction half of the material is decomposed in 1000 seconds. How long will it be until only one-third is left?
8. At 400°C, the first order conversion of cyclopropane to propylene has a rate constant of 1.16×10^{-6} s^{-1}. If the initial concentration of cyclopropane is 1.00×10^{-7} mol L^{-1} at 400°C what will its concentration be 20.0 hours after the reaction begins?
9. At 27°C the following data were obtained for the reaction

$$2NOCl \rightarrow 2NO + Cl_2$$

Experiment	Initial concentration of *NOCl* (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1	0.30	3.60×10^{-9}
2	0.60	1.44×10^{-8}
3	0.90	3.24×10^{-8}

(a) What is the rate law for this reaction?

(b) What is the rate constant?

(c) By what factor would the rate increase if the initial concentration of *NOCl* were changed from 0.30 mol L^{-1} to 0.45 mol L^{-1}?

10. What are the characteristics of first and second order reactions?
11. How did Arrhenius explain the temperature dependence of reaction rates? Briefly discuss his theory.
12. The results for the decomposition of N_2O on gold surface at 900°C are as follows:

Time (in minute)	30	53	65	80	100	120
% decomposition	32	50	57	65	73	78

Show that the reaction is of first order and calculate the velocity constant.

13. The kinetic data for the reaction between sodium thiosulphate and methyl iodide at 25°C are as follows (the concentrations are expressed in arbitrary units)

Time (in minute)	0	4.75	10	20	35
$[Na_2S_2O_3]$	35.35	30.5	27.0	23.2	20.3
$[CH_3I]$	18.25	13.4	9.9	6.1	3.2

Show that the reaction is of second order and calculate the mean specific rate constant.

14. What is meant by order of a chemical reaction and how can it be determined experimentally?
15. What do you understand by the order of a reaction? Discuss three methods for the determination of the order of a reaction.
16. What is the difference between the order and molecularity of chemical reactions?
17. (a) Deduce an expression for the velocity constant of a second order gas reaction.
    (b) In a certain first order reaction, half of the material is decomposed in 1,000 secs. How long will it take for only one-tenth to be left?
18. (a) Distinguish between the velocity of a reaction and its specific reaction rate.
    (b) Show that in a first order reaction the time of half decomposition is independent of the initial concentration.
    (c) The specific reaction rate for a first order reaction is 0.0635 per minute. Calculate the time for half reaction.

19. Assuming the initial concentrations of two reactants in a second order reaction to be same, derive a rate expression.
20. What are the units of the specific reaction rates for a first order and a second order reaction? From this discuss how the *k* values will change with change of unit of concentration.
21. A first order reaction is never complete. Give justification for the statement.
22. The rate constant for the reaction

$$CH_3I\,(g) + HI\,(g) \rightarrow CH_4\,(g) + I_2\,(g)$$

at 200°C is 1.32×10^{-8} L mol $^{-1}$ s^{-1}. At 275°C the rate constant is 1.64 L mol $^{-1}$s^{-1} Calculate the activation energy (in kJ per mole) and the value of *A*.

23. The activation energy for the reaction is 182 kJ mol^{-1}.

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$

The rate constant for the reaction at 700°C is 1.57×10^{-3} L mol $^{-1}$ s^{-1}. What is the value of the rate constant at 600°C?

24. A mechanism for the reaction: $2NO + Br_2 \rightarrow 2NOBr$ has been suggested as follows:

Step 1 $NO + Br_2 \rightarrow NOBr_2$

Step 2 $NOBr_2 + NO \rightarrow 2NOBr$

   (a) What would be the rate law for the reaction if the first step in this mechanism were slow and the second step a fast equilibrium?
   (b) What would be the rate law if the second step were fast and the first step a fast equilibrium?
   (c) Experimentally the rate law has been found to be rate = $k\,[NO]^2[Br_2]$
   What can be deduced about the relative speeds of step 1 and step 2 from this rate law?
   (d) Why do we not prefer a simple, one step mechanism

$$NO + NO + Br_2 \rightarrow 2NOBr$$

   (e) Can we, on the basis of the experimental rate law, definitely exclude the mechanism in part (d)

25. Outline collision theory of reaction rates. How is the energy of activation attained by reactive species? What are productive and unproductive collisions?
26. What are meant by 'Activated Complex' and 'Energy of Activation'? Describe how you would account for endothermic and exothermic reactions in terms of the potential energy diagram.
27. What are chain reactions and why are they so called? Illustrate your answer with suitable examples.
28. What are the characteristics of a chain reaction? When does a chain reaction result in explosion?
29. Discuss Beer-Lambert's law and deduce a mathematical expression for the law. What are the applications of this law? What are the limitations of Beer-Lambert's law?
30. What is meant by the law of photochemical equivalence? Explain the term 'quantum yield' in a photochemical reaction. What information can be obtained from quantum yield?
31. Explain clearly the explosion limits in hydrogen-oxygen reaction. Give a suitable diagram.
32. Deduce a kinetic expression for a heterogeneous reaction in terms of Langmuir's concept of unimolecular layer.
33. How does the order of a reaction vary with the extent of surface covered by the reactant. Explain your answer by appropriate mathematical relations.
34. In the decomposition of gaseous hydrogen iodide over a temperature range of 556 – 781 K the rate constants are as follows:

$$k_{556} = 3{\cdot}517 \times 10^{-7}\ \text{mol}^{-1}\ \text{sec}^{-1}$$
$$k_{781} = 4.954 \times 10^{-2}\ \text{mol}^{-1}\ \text{sec}^{-1}$$

From the above result calculate the energy of activation for the reaction. [Ans. 186.4 kJ]

13 CATALYSIS

It has been mentioned (Chapter12) that chemical reactions can be greatly influenced by the presence of a foreign material in the reaction mixture. The rate of reaction can be increased or decreased and in many cases the very course of a reaction can be changed by introducing foreign bodies in reacting systems. The foreign body can be recovered and remains chemically unchanged at the end of the reaction. Such foreign bodies are known as *Catalysts*. The cases where there is an acceleration or retardation of the reaction rate but no change in the reaction course shall comprise this chapter. The original definition of catalyst due to Berzelius (1836) implies that reactions are influenced by unknown force from the foreign body. Although this concept is no longer valid, the term catalyst is still retained.

13.1 Definition

A catalyst is a chemical entity which by virtue of its presence in a reacting system increases or decreases the rate of the reaction, itself remaining unchanged in chemical properties or mass at the end of a reaction. The phenomenon of alteration of the rate of a reaction by a catalyst is known *catalysis.*

A catalyst which increases the rate of the reaction is said to be a *positive catalyst.* In most cases catalysts are used to increase the rate of reactions and our discussion will be mainly about positive catalysts. If, however, a catalyst decreases the rate of a reaction it is called a *negative catalyst.* Negative catalysts find application in controlling undesirable side reactions. In some reactions one of the products formed during the reaction acts as a positive catalyst for the overall reaction. Such a phenomenon is called *autocatalysis.* When $KMnO_4$ is slowly added to a solution of oxalic acid the pink colour of the permanganate is discharged slowly at first (*reaction is slow*), but after a certain volume of the permanganate solution has been added the colour is discharged very rapidly (*reaction is fast*), i.e. some species formed as a result of the reaction act as catalyst for the reaction.

13.2 Types of Catalysis

Catalysis has been divided into three types :

Homogeneous catalysis,
Heterogeneous catalysis and
Enzyme catalysis (Biological catalysts)

13.2.1 Homogeneous catalysis

In a reaction if the catalyst is present in the same phase as the reactants, it is called a *homogeneous catalyst* and the phenomenon is *homogeneous catalysis.* Such catalysis can take place in gaseous reaction or reactions in solution. This type of catalysis can some times be explained in terms of the formation of an intermediate compound or ion or a radical. Examples of homogeneous catalysis in the gas phase are:

(a) Oxidation of sulphur dioxide, SO_2, by oxygen to sulphur trioxide, SO_3, in presence of nitric oxide, NO, in the Chamber Process for sulphuric acid manufacture.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Here NO acts as a catalyst.

(b) The following reaction in the gas phase is catalysed by traces of chlorine gas, particularly in presence of light.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

In presence of light chlorine forms chlorine radicals, which react with N_2O forming the intermediate radical $ClO\bullet$. The proposed mechanism is

$$\begin{array}{llcl} \textit{Step 1} & N_2O(g) + Cl\bullet(g) & \rightarrow & N_2(g) + ClO\bullet(g) \\ \textit{Step 2} & 2ClO\bullet(g) & \rightarrow & Cl_2(g) + O_2(g) \end{array}$$

(c) Some examples of homogeneous catalysis in solution are as follows:

(i) Hydrolysis of ester in presence of acid or alkali.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5(l)} + H_2O(l) \rightarrow \underset{\text{acetic acid}}{CH_3COOH(aq)} + \underset{\text{ethyl alcohol}}{C_2H_5OH(aq)}$$

(ii) Hydrolysis of sucrose (cane sugar) into glucose and fructose in presence of mineral acids acting as catalyst.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

(iii) Reaction of acetone with iodine in presence of mineral acid which acts as a catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + HI(aq)$$

13.2.2 Heterogeneous catalysis

If in a catalyzed reaction the catalyst itself is in a different phase from the reactants the phenomenon is called *heterogeneous catalysis.* In heterogeneous catalysis the reactions take place at the interface of two phases. The catalyst is often a solid and adsorbs a liquid or a gas. This type of catalysis is of great importance in many industrial processes. Examples are :

(i) Manufacture of ammonia by the Haber process. Iron (Fe) acts as catalyst.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

(ii) Manufacture of sulphuric acid by the Contact process. Vanadium pentoxide (V_2O_5) or platinum are catalysts for the production of $SO_3(g)$ from $SO_2(g)$ and $O_2(g)$.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

(iii)Nickel or platinum as catalyst for the hydrogenation of oils and fats.

(iv)Catalysts used in many reactions in the petroleum and polymer industries.

There are cases of heterogeneous catalysis where a reaction in the liquid phase is catalyzed by a substance in the solid state. An example is the decomposition of H_2O_2 (aqueous) by $MnO_2(s)$.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Again there are examples of reactions in which both the reactant and the catalyst are in the solid phase. The decomposition of $KClO_3$ is catalyzed by solid MnO_2.

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

13.3 Characteristics of Catalysts

The following characteristics are common to most of the catalytic reactions even though the types may be different.

(a) The catalyst remains unchanged in mass and chemical properties at the end of a reaction. However, the catalyst may undergo some changes in physical appearance and forms. Compact lumps of MnO_2 used as a catalyst for the thermal decomposition of $KClO_3$ is found to fall to powder at the end of the reaction. Platinum surface, used as a catalyst for hydrogen-oxygen reaction, is found to be coated with a deposit when the reaction is over.

(b) Usually a small amount of the catalyst is sufficient to bring about a large change. This is quite obvious because the catalyst is not present in the product of the reaction, i.e., it is not chemically consumed. Unless a heterogeneous catalyst is poisoned or a homogeneous catalyst is chemically destroyed or lost, the catalysts can be used over and over again bringing about a considerable amount of reaction. In many reactions a trace of the catalyst is sufficient to bring about a large change in a relatively short time. In some cases, however, a relatively large amount of the catalyst must be present to make significant change in the rate. For example, in the *Friedel-Crafts reaction* the catalytic activity of solid anhydrous aluminum chloride is increased significantly if it is added in large quantity to the reaction mixture.

$$C_6H_6(l) + C_2H_5Cl(l) \rightarrow C_6H_5C_2H_5(l) + HCl(g)$$

(c) *A catalyst does not alter the final position of equilibrium.* This is because the catalyst alters the rate of the forward and reverse reactions to the same extent leaving the position of equilibrium unchanged; the time for attainment of the equilibrium is only altered. This condition is in conformity with energy considerations.

(d) *A catalyst cannot, in general, start a reaction.* Some reactions, however, cannot start in absence of the catalyst. An example is the reaction between $H_2\,(g)$ and $O_2\,(g)$ which can be kept together at room temperature for many years without reaction taking place. The presence of traces of platinized platinum, however, starts the reaction very quickly.

Some scientists believe, mainly from experimental studies, that a catalyst can start a reaction. One way of reconciling the opposite views is to consider the reaction rate to be infinitely slow. The case is, however, more complicated. In such reactions the catalyst at first reacts chemically with one of the components forming a highly reactive species, which then brings about the chemical reaction. In absence of the catalyst the reaction cannot occur. This class of catalysts should be termed `*initiators*'. An example is the use of organic peroxides as initiators in polymerization reactions. The peroxide is thought to split into free radicals which initiate the reaction.

$$ROOR \rightarrow 2RO\bullet$$

$$RO\bullet + CH_2 = CH_2 \rightarrow ROCH_2CH_2\bullet$$

$$ROCH_2CH_2\bullet + CH_2 = CH_2 \rightarrow ROCH_2CH_2CH_2CH_2\bullet$$

(d) *A catalyst is specific in its action.* All material bodies cannot act as catalysts in all reactions. A suitable catalyst for a particular reaction is to be found out by trial and error because with our present knowledge a prediction as to the *specificity* of a catalyst cannot be made. Examples are the different catalysts for different reactions described so far. A catalyst which can be highly reactive in a certain reaction may not be of any use in another reaction.

Extensive research in the field of catalysis has yielded results from which the following claims are *now* made :

Catalysts can be designed to

(i) help initiate reaction;
(ii) stabilize the intermediates of a reaction;
(iii) hold the reactant molecules close to each other;
(iv) hold the reactant molecules in the right orientation on the catalyst;
(v) block side reactions;
(vi) make bonds easier to break;
(vii) donate and accept electrons and
(viii) act as efficient means for energy transfer.

13.4 Energy Changes in Catalytic Reactions

The question may arise as to how does the catalyst enhance the rate of reactions? This can be explained with the help of an energy diagram as in Figure 13.1. It has been shown that a catalyzed reaction has a lower activation energy than the same reaction taking place in the absence of the catalyst. This is possible if the catalyst provides an alternative route for the reaction with lower activation energy. Figure 13.1 shows that the enthalpy change for the reaction, $\Delta H_{reaction}$, is not affected by the presence of the catalyst. *It should be recognized that the catalyst does not lower the activation energy.* A catalyst provides a different route with lower activation energy.

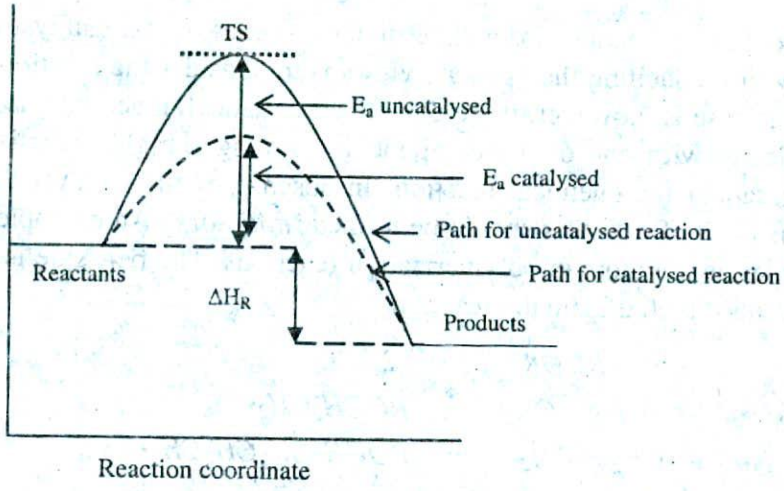


Figure 13.1 Energy diagram for uncatalysed and catalysed reactions

In Figure 13.1 the uncatalysed reaction is shown as a single step with high energy of activation. The catalyzed reaction is shown as a two-stage process with lower activation energy and is, therefore, faster. It is possible that the uncatalysed reaction proceeds by more than one step and the catalyzed reaction may also consist of several steps. The important point to note is that for the catalyzed reaction there is no step which has higher activation energy than the uncatalysed reaction. It may be noted that the $\Delta H_{reaction}$ is the same (Figure 13.1), since energies of the reactants and the products remain unchanged in the presence of the catalyst.

If, however, the reaction is reversible, the catalyst equally decreases the energy of activation of the forward reaction and reverse reaction. Thus, the rate of the forward reaction is accelerated to the same extent as that of the reverse reaction. As a result the equilibrium is quickly established, but the position of equilibrium remains unchanged. Effect of catalyst on some reactions is given in Table 13.1.

Table 13.1 Activation energy of some reactions

Substances decomposed	Uncatalysed reaction	Catalysed Reaction	
	E_a kJ mol^{-1}	Catalyst surface	E_a kJ mol^{-1}
Methyl ethyl ether	227.8	Pt	158.8
Diethyl ether	221.5	Pt	143.4
Hydrogen iodide	183.9	Pt	58.5
Hydrogen iodide	183.9	Au	104.5
Nitrous oxide	244.5	Au	121.2
Ammonia	334.4	W	163.0

13.5 Promoters and Catalytic Poisons

***Catalytic promoter**: Promoters are substances which when mixed with the catalyst increases its catalytic activity.* These substances themselves are not catalysts for the reaction. A small quantity of promoter is sufficient to increase the activity of the catalyst to a large extent. Few examples are:

(i) In the Haber-Bosch process for the synthesis of ammonia, small amounts of molybdenum, high melting oxides of some metals like aluminium, chromium, rare earths etc. are found to increase the activity of the iron catalyst considerably. For this reason in industry iron alone is not used but is always mixed with a suitable promoter.

(ii) In the hydrogenation of vegetable oils the nickel catalyst is used along with promoters like copper and tellurium.

***Catalytic poisons:** Substances which, by their presence, reduce the catalytic activity of a catalyst are called catalytic poisons.* Examples are:

(i) Carbon monoxide gas acts as a poison when present during the hydrogenation of alkenes with finely divided nickel as a catalyst.

(ii) The catalytic activity of platinum in the oxidation of SO_2 to SO_3 in the contact process for the manufacture of sulphuric acid is poisoned by the presence of arsenic, dust particles etc.

The mechanism of action of catalytic poisons and promoters will be discussed later.

13.6 Theories of Mechanism of Catalysis

Two main theories for the action of catalyst on rates of reaction have been proposed. These try to explain how the catalyst provides an alternative pathway for the reaction by altering the mechanism.

(a) Intermediate compound theory: The essential feature of the theory is that the catalyst chemically combines with one of the reactants to form an unstable active intermediate compound which then reacts further with the other reactants giving the final product and the catalyst is regenerated. In some reactions the intermediate compound can be easily detected and even isolated whereas in some reactions the existence of the intermediate compound can be proved by sophisticated methods alone. Some examples are shown below :

(i) As shown earlier the oxidation of SO_2 to SO_3 by NO in presence of oxygen or air is known to occur by the following sequence of reactions :

$$\begin{aligned} 2NO + O_2 &\rightarrow 2NO_2 \\ 2NO_2 + 2SO_2 &\rightarrow 2SO_3 + 2NO \\ 2NO + 2SO_2 + O_2 &\rightarrow 2SO_3 + 2NO \qquad \text{net reaction} \end{aligned}$$

However, in the absence of NO the oxidation is extremely slow. NO then may be looked upon as an '*oxygen carrier*'.

(ii) In the oxidation of iodides by hydrogen peroxide and the oxidation of iodides in acid medium by oxygen, hypoiodous acid (or more correctly speaking IO^-) is the intermediate active species that is responsible for the reaction.

$$\begin{aligned} H_2O_2\,(aq) + I^-\,(aq) &\rightarrow H_2O\,(l) + IO^-\,(aq) \\ H_2O_2\,(aq) + IO^-\,(aq) &\rightarrow H_2O\,(l) + O_2\,(g) + I^-\,(aq) \end{aligned}$$

(iii) In the reaction between benzene (C_6H_6) and ethanoyl chloride (CH_3COCl) giving phenyl methyl ketone, $C_6H_5COCH_3$, anhydrous $AlCl_3$ is used as a catalyst.

$$C_6H_6\,(l) + CH_3COCl\,(l) \rightarrow C_6H_5COCH_3\,(l) + HCl\,(g)$$

$AlCl_3$ first reacts with ethanoyl chloride giving rise to an intermediate species, $CH_3CO^-.\ AlCl_4^+$, which then reacts with benzene and phenyl methyl ketone is formed. $AlCl_3$ is regenerated.

$$\begin{aligned} CH_3COCl + AlCl_3 &\rightarrow CH_3CO^-.\ AlCL_4^+ \\ C_6H_6 + CH_3CO^-.\ AlCl_4^+ &\rightarrow C_6H_5COCH_3 + AlCl_3 + HCl \end{aligned}$$

The intermediate compound theory has been found useful in many reactions, particularly in homogeneous catalysis.

(iii) Acid catalysis of ester hydrolysis is another example where an intermediate is supposed to be formed. The case of hydrolysis of an ester such as methyl acetate in water may be considered.

$$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$$

The reaction is slow but the presence of an acid makes the reaction proceed at a much faster rate.

(b) Adsorption theory: This theory can be applied to heterogeneous catalysis only. As the name suggests the reactant is *adsorbed* on the surface of the catalyst and the effective concentration of the reactant is generally increased on the surface, the reactants are brought closer and the reaction speed is increased. However, it is now fairly well known that simple *physical adsorption* (see *Section 18.3*) on the surface of the solid has practically nothing to do with catalysis. It is *chemisorption* that is mainly responsible for catalytic activity. As mentioned the unused bonding capabilities of the surface atoms or ions may be utilized to bond molecules from the gas or solution phase to the surface of the solid. In practice not all the atoms or ions on the surface are reactive and can adsorb gases or ions. The places where reacting molecules can get adsorbed are called ***active sites***. The extent of chemisorption will, therefore, depend on the number of available active sites and on the nature of the reacting molecules. The number of active sites per unit of catalyst depends on the nature of the catalyst, on its method of preparation, and on its treatment before use.

It is believed that the mechanism of heterogeneous catalysis on the surface of solid catalysts consists of five steps as follows:

(i) ***Diffusion:*** Reactant molecules diffuse to the solid catalyst surface.

(ii) ***Adsorption:*** Reactant molecules are first physically adsorbed on the surface. They then become chemisorbed.

(iii) ***Chemical reaction:*** The chemisorbed molecules adjacent to each other react to produce the products.

(iv) ***Desorption:*** This is the reverse of adsorption. After the reaction the product molecules are at first chemisorbed on the surface. They then become physically adsorbed and finally break free from the surface.

(v) ***Diffusion:*** The product molecules diffuse away from the surface.

The five steps are illustrated in Figure 13.2 for the catalytic hydrogenation of ethylene to form ethane using finely divided nickel catalyst.

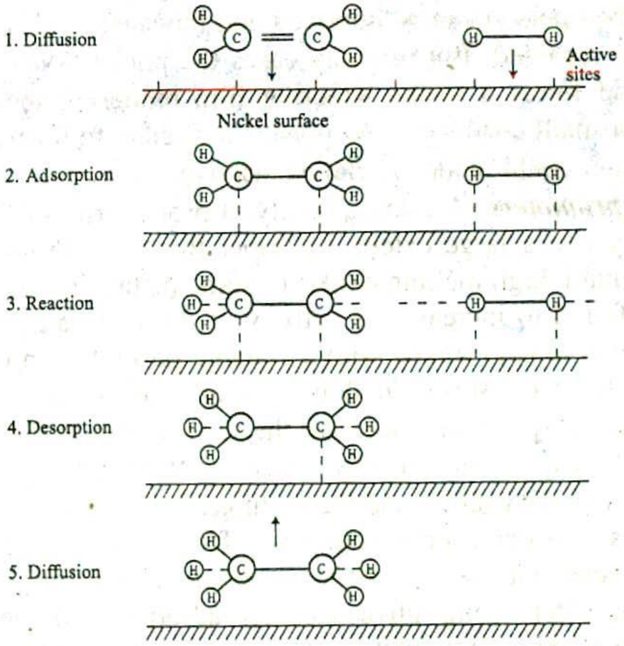


Figure 13.2 : Schematic diagram of five steps in heterogeneous catalysis

Both ethylene and hydrogen molecules diffuse (*step i*) to the catalyst surface and then gets adsorbed on the surface (*step ii*). The adsorption of hydrogen molecule results in gradual breaking of $H-H$ and the formation of two $M-H$ bonds where M is the metal surface (*step iii*). These are termed '*surface compounds*' which are unstable and highly reactive. Ethylene molecules are also chemisorbed to form 'surface compounds'. These should be oriented in a definite manner on the surface leaving a part of the molecule, i.e. atom or atoms of the molecule in a condition favourable to the reaction. If the $M-H$ bond is relatively weak the hydrogen atoms may move about on the metal surface. When they encounter an ethylene molecule the hydrogen atoms may become bound to the carbon atoms (*step iv*) forming the ethane molecule. The ethane molecule is now released from the metal surface and diffuses away from the surface (*step v*). The active site is now ready to adsorb fresh molecules of the reactants.

The adsorption theory satisfactorily explains the following :

(i) ***The specific nature of the catalyst and the change in the course of reaction by changing the surface:*** When the surface material is changed the nature of chemisorption of the molecules is changed and different reaction products are expected. When ethyl alcohol is decomposed on Al_2O_3 surface, the principal products are C_2H_4 and H_2O – a case of dehydration. In the presence of copper the principal products are acetaldehyde and hydrogen, a case of dehydrogenation. *Fe* or *Pt* is specific in their action as catalyst in the synthesis of ammonia.

(ii) The action of catalytic poisons: These substances are strongly adsorbed on the catalyst surface- more so on the active sites-, and thus the surface is made unavailable for chemisorption of the reacting gas. The catalytic activity is, therefore, lost. In temporary poisoning the adsorbed poison can be removed and the surface cleaned rather easily and the catalytic activity regained. But in many cases the poison forms surface compounds with the catalyst and forms a strong adhering film rendering the catalyst completely inactive. Thus only a small quantity of the poison, sufficient to form a unimolecular layer of 'surface compounds', could render a catalyst inactive.

(iii) The role of promoters: A small quantity of promoter is sufficient to increase the activity of the catalyst to a large extent. In Haber-Bosch synthesis of ammonia, small amounts of molybdenum, high melting oxides of some metals like aluminium, chromium, rare earths etc. are found to increase the activity of the iron catalyst considerably. Iron alone is not used but is always mixed with a suitable promoter. In the hydrogenation of vegetable oils the nickel catalyst is used along with promoters like copper and tellurium.

It is suggested that the promoter increases the surface area of the catalyst by reducing the *'particle size'* of the catalyst and also by increasing the number of active sites.

It is also possible that the catalyst and the promoter form a loose type of compound and this compound offers a better chemisorption site for the reacting molecules. This may roughly explain the selectivity of the promoter action. It may also be possible that the catalyst-promoter pair offers competitive sites for adsorption to the molecules and the different atoms of the reacting molecules are chemisorbed on both the surfaces leaving the adsorbed molecules in a highly strained active form, thus enhancing the reaction rate.

13.7 Acid-Base Catalysis

Many organic reactions in solution are known to be catalyzed by acids or bases or both. These reactions form an important class of homogeneous catalytic reactions and the phenomenon is treated as general *acid-base catalysis*. In acid-base catalysis either the catalyst remains absolutely unchanged in concentration at the end of the reaction, or the catalyst is progressively consumed during the reaction, the consumption of the catalyst being a measure of the extent of the reaction. In the latter case the catalyst directly reacts with one of the products formed. Examples of acid-base catalysis are:

(a) Hydrolysis of sucrose by an acid in aqueous medium

(b) Hydrolysis of an ester, e.g., methyl acetate, ethyl acetate etc. are catalyzed by acids.

In such reactions the specific reaction rate is influenced by acid concentration or, more strictly speaking, by the hydrogen ion concentration. All the above reactions are first order processes. In some of the reactions not only the hydrogen ion but also the undissociated molecules of the acid act as catalysts.

Similarly, the rates of many reactions involving hydrolysis are enhanced by the OH^- ion of the base. The decomposition of di-acetone alcohol by sodium hydroxide in aqueous solution is an example. The reaction follows first order kinetics. Hydrolysis of ethyl acetate by sodium hydroxide is, however, a second order process, the alkali reacting with the acetic acid formed to give sodium acetate.

In such reactions there are examples when the undissociated molecules also enhance the rate of reaction. Thus we have general base catalysis. In some reactions both acids and bases are found to catalyze the reactions. However, there are instances where only the acid (H^+) or only the base (OH^-) is effective. Acetal and sucrose are decomposed only by H^+ ion. The hydrolysis of ethyl ortho carbonate is also catalyzed by H^+ ion only. On the other hand, hydrolysis of diacetone alcohol and decomposition of nitramide are enhanced by the OH^- ion or anions of weak acids. However, the effect of OH^- ion predominates over any other effect. These actions are really specific catalysis.

13.8 Mechanism of Acid-Base Catalysis

The addition of proton or its removal must be associated with acid-base catalysis; this is because for most cases an acid may be treated as a proton donor and a base as proton acceptor. A general mechanism may, therefore, be represented as

$$AB + H^+ \rightarrow ABH^+ \rightarrow BA + H^+$$

where AB is a molecule undergoing a change in acid solutions, giving a different entity BA. Mutarotation of glucose by H^+ or OH^- follows the above pattern. In many other reactions involving hydrolysis by acids and bases the same mechanism may be assumed to be followed.

Experimental evidences support that the acid-catalyzed reaction consist of many protonation and deprotonation steps.

Water is known to undergo dissociation giving H^+ and OH^-. Water itself may, therefore, bring about hydrolysis and it does so. On addition of an acid its proton donating power increases since $H^+ + H_2O \rightarrow H_3O^+$. Similarly, on addition of a base its proton accepting power increases.

13.9 Enzyme Catalysis

Many chemical reactions associated with living organisms are accelerated by a group of closely related substances called enzymes. Enzymes play a dominant role in biochemical reactions responsible for our digestion and metabolism of food stuff and thousands of other reactions taking place in our body every second. Enzymes are also important in a number of industrial processes like making wine and beer, manufacture of foods, pharmaceuticals, detergents etc. Enzymes are proteinous materials of complex organic structure having molecular masses of 10,000 or above. Many of them can now be obtained in pure crystalline forms. Like other catalysts they influence the reaction rates when present in small quantity by providing an alternative path with a lower activation energy. Many enzymes require the presence of other non-protein substance before they can function well. These are called coenzymes. They could be organic compounds or metal ions.

Some examples of enzyme catalysis are shown in the Table below :

Table 13.2 Some enzymes and their functions

Enzymes				***Functions***
Amylase	Converts	Starch $(C_6H_{12}O_5)_n$	into	Sugar $C_{12}H_{22}O_{11}$
Catalase	Converts	H_2O_2	into	$O_2 + H_2O$
Invertase (in yeast)	Converts	Sucrose $C_{12}H_{22}O_{11}$	into	Glucose + fructose $C_6H_{12}O_6 + C_6H_{12}O_6$
Zymase (in yeast)	Converts	Glucose $C_6H_{12}O_6$	into	Ethanol + Carbon dioxide $C_2H_5OH + CO_2$
Urease(*in soya bean*)	Converts	Urea H_2NCONH_2	into	Carbon dioxide + Ammonia $CO_2 + NH_3$
Papain(*from Papaya*)	Converts	Beef	into	Tender

Enzymes have a number of characteristic properties that make them efficient and specific catalysts for many biological reactions. The important ones are mentioned below.

(a) ***Selectivity:*** Enzymes are very selective in their action. This specificity makes enzymes very effective and useful in biological reactions. A particular enzyme catalyses a specific reaction out of a number of possible reactions. For example, urease (found in soya beans) catalyses the hydrolysis of urea (carbamide) but not a substituted amide.

$$H_2NCONH_2 + H_2O \rightarrow CO_2 + 2NH_3$$

(b) Efficiency: Even a small quantity of the enzyme can bring about a large amount of change in a reaction. For example, in one second one molecule of catalase decomposes about 50,000 molecules of hydrogen peroxide. This is possible because the enzyme molecule is regenerated very quickly during its catalytic activity. As will be seen below the mechanism of catalytic action of the enzymes makes this quick regeneration possible.

(c) Size: As mentioned earlier the relative molecular masses of enzyme are very large and range from 10,000 upwards. These dimensions (i.e., the size of the molecule) are in the colloidal range and cannot be classified as homogeneous or heterogeneous. They fall somewhere in between.

(d) Temperature: Enzymes operate with maximum efficiency in a small range of temperature, usually around 37°C, which is the body temperature of a healthy person. If the temperature is increased to 50°C or more enzymes become inactive.

(e) pH of the solution: The *pH* of the medium has profound effect on the catalytic activity of an enzyme. The efficiency of an enzyme is maximum at a particular *pH*, called the *optimum pH*. Most biological enzymes are most efficient at a *pH* of about 7.4. This is the *pH* of blood and most other body fluids.

(f) Poisons: Enzymes are very sensitive to the presence of substances which may reduce (inhibit) or completely destroy their catalytic activity. These are called poisons, like other catalytic poisons. In the fermentation process for the preparation of ethanol, fermentation stops if the concentration of ethanol exceeds 5.5%.

13.10 Mechanism of Enzyme Catalysis

The substance on which the enzyme acts is called the *substrate*. The enzyme molecule is a protein chain that acquires a shape such that the substrate can fit into its structure somewhat like a *lock-and-key* arrangement as shown in Figure 13.3. The enzyme molecule, *E*, binds the substrate, *S*, into the active sites of its structure to form an enzyme-substrate complex, *ES*, and catalysis takes place.

In effect the active site in the enzyme 'recognizes' the substrate. This explains the specificity characteristic of enzymes. The enzyme-substrate complex then breaks up to form the product, *P*, and the

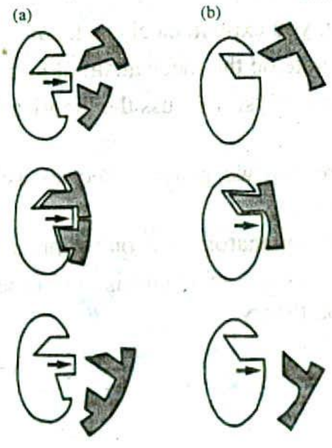


Figure 13.3 Schematic diagram of lock-key mechanism. (a)An enzyme can join two molecules (b) an enzyme can alter the structure of a molecule

enzyme is regenerated and is ready to react with another molecule of the substrate. The mechanism is shown as

$$E + S \rightleftharpoons ES \rightarrow P + E$$

The formation of the enzyme-substrate complex provides a new pathway with a lower activation energy.

When inhibitors occupy the active sites or temperature is increased with loss of structure of the enzyme (it being a protein) the catalytic action of the enzyme is lost.

The *lock-and-key model* of enzyme action is now firmly established by many experiments. Consideration of the kinetics of enzyme catalysed reactions is beyond the scope of this text.

QUESTIONS AND PROBLEMS

1. Write an essay on homogeneous catalysis illustrating your answer with suitable examples.
2. Define a catalyst and mention clearly the criteria for catalysis.
3. What is the intermediate compound theory of catalysis? Is this theory universally applicable? Justify your answer.
4. How can you explain catalysis on the basis of the adsorption theory?
5. What are the essential features associated with heterogeneous catalysis? Give some examples of industrially important catalyzed reactions.
6. Write a short essay on acid-base catalysis.
7. Explain with the help of a mathematical expression the effect of enzymes on enzyme-catalyzed reactions.

R. How can you explain catalysis from your knowledge of the potential energy diagram ?

9. Write a note on the mechanism of homogeneous catalysis.
10. Define a catalyst. Discuss the theories associated with catalysis with special reference to heterogeneous systems.
11. What are the two general theories associated with catalysis? Discuss the two theories with suitable examples.
12. Write an explanatory note on the phenomenon of catalysis in gaseous reactions.
13. Write an essay on catalysis with special reference to the adsorption and intermediate compound formation theory.

14 ELECTRICAL CONDUCTANCE AND ELECTROLYSIS

Substances through which electricity can flow are called electrical conductors. Substances which do not conduct electricity at all are termed *insulators*. Metals, graphite or solutions of salts, acids and bases conduct electricity. Metals conduct electricity in the solid and molten state. Graphite is the only non-metal which conducts electricity and that only in the solid state. Conduction of electricity by metals and solutions of salts acids and bases has been known for a long time. Salts conduct electricity also in the molten state. Electrical conduction by chemical compounds in solution and in the molten state is accompanied by physical and chemical changes. The phenomenon of chemical change by the passage of electricity through substances in solution or the molten state is called *electrolysis*.

14.1 Electrolytic Conduction

Conductors of electricity may be divided into two groups according to the mechanism by which electricity is carried through them.

(a) *The electronic conductors* where electricity is carried by *electrons*. Metals and graphite fall in this category.

(b) *The electrolytic conductors* where the electric current is carried by *ions*. Solutions of acids, bases and salts fall in this category. Substances which conduct electricity in solution are called electrolytes.

Examples are known of cases where the current is carried partly by *electrons* and partly by *ions*.

The capacity of conducting electricity is not the same for all electrolytes. *Strong electrolytes* are those which are good conductors of electricity whereas those electrolytes which are poor conductors are called *weak electrolytes*. The distinction between the two types is rather vague. Salts, mineral acids and hydroxides of alkali and alkaline earth metals are grouped as strong electrolytes. Organic acids, ammonium hydroxide etc. are weak electrolytes.

14.2 Metallic and Electrolytic Conduction

There are several points in which metallic conduction and electrolytic condition differ. The following Table gives a comparison of the two types of conduction of electricity.

Table 14.1 Comparison of metallic conduction and electrolytic conduction

	Metallic conduction		*Electrolytic conduction*
(i)	The current is solely carried by the electrons in the conduction band (*Section 4.11.3*).	(i)	The current is carried by both cations and anions.
(ii)	The velocity of the electrons is very large.	(ii)	Ionic velocities are much smaller than electron velocities.
(iii)	During passage of current no chemical reaction occurs; only heating effect is produced.	(iii)	Passage of current brings about chemical reactions; heat is also evolved.
(iv)	Specific conductance of many metals are quite high; they are very good conductors of electricity.	(iv)	Specific conductance is low; they are moderately good conductors.
(v)	Temperature co-efficient in general is negative (alloys show complex behaviour).	(v)	Temperature co-efficient is positive.
(vi)	Ohm's law applies.	(vi)	Ohm's law applies.
(vii)	Conductance may be measured by *d-c* or *a-c* current.	(vii)	Conductance is measured by *a-c* source; *d-c* current can be used only by elaborate arrangements.

14.3 Electrolysis

Early in the investigation on the effect of passing current through solutions it was discovered that decomposition of the solute took place. As soon as the current stopped decomposition ceased, clearly indicating that the decomposition was in some way connected with the passage of the current. Also the products appeared only at the poles where the electricity entered or left the solution. M. Faraday (1832-33) studied the phenomena associated with electrolysis and introduced the nomenclature which is used to-day. The pole, usually wires or plates, through which the electricity was supposed to enter the solution was termed *cathode* and the pole where it was supposed to leave the solution was called the *anode*; the former is the one attached to what is known by convention as the `positive pole' of the battery and the latter is attached to the `negative pole'. The cathode and anode are termed the *electrodes*. Faraday assumed the flow of electricity through solutions to be associated with the movement of charged particles; these were called ions (Greek: wanderer). He, however; did not say anything about their origin. The particles carrying a positive charge and moving towards the cathode were referred to as *cations* and the ones carrying a negative charge and moving towards the anode were referred to as *anions*. On reaching the electrodes the charges on the ions were thought to be neutralized and the particles deposited in the form of atoms or molecules.

14.4 The Mechanism of Electrolytic Conduction

The first successful mechanism of electrolysis was put forward by R. Clausius (1857). He made the following assumptions:

(i) in solution the electrolytes are automatically split into ions,

(ii) the ions exist only for a short interval and an equilibrium exists between the ions and the undissociated molecules,

(iii) the free ions carry charge and carry current during the short period of their existence.

(iv) only a very small number of the molecules would be split up into ions,

(v) as the ions are removed by discharge at the electrodes or recombination, fresh molecules break up into the ions in order to maintain the equilibrium.

This theory was satisfactory to a large extent, but there was no quantitative expression associated with it. The quantitative relationship was given by Arrhenius.

S. Arrhenius put forward his theory of electrolytic dissociation in 1887. According to this theory it is assumed that when an acid, base or salt is dissolved in water, a fraction of it breaks up spontaneously into positive and negative ions, and an equilibrium is established between the undissociated electrolyte molecules and the ions. Thus for the electrolyte MA,

$$MA(\mathrm{aq}) \rightleftharpoons M^{+}(\mathrm{aq}) + A^{-}(\mathrm{aq}) \qquad (12.1)$$

The ions are free to move independently and randomly in the liquid medium. When an electric field is applied the ions are attracted towards the electrodes, the positive ions, called *cations,* going to the cathode and the negative ions, called *anions,* to the anode. At the electrodes the ions give up their charge and are liberated. By postulating that the fraction of the electrolyte dissociated increased when the solution was diluted Arrhenius was able to explain the concentration variation of conductance. Arrhenius gathered support for his theory from van't Hoff's investigation of the colligative properties of solutions (*Section 9.20*).

It is now believed that once electrolytes are placed in water the ions separate. The ions get surrounded by water molecules and oppositely charged ions which form what is called an ion atmosphere. When electricity is passed through the solution ions with their ion atmospheres move to electrodes with opposite sign (*Section 14.13*).

14.5 Faraday's Laws of Electrolysis

Micheal Faraday (1804) carried out a large number of experiments on electrolysis, and derived quantitative relationships between the quantity of electricity passed through the electrolyte and the amount of material liberated on the electrodes. The results of his experiments were expressed in the form of two laws. These are known as Faraday's Law of electrolysis

First Law of Electrolysis: *The amount of substance dissolved from or liberated at an electrode is proportional to the quantity of electricity passed through the electrolyte solution.*

The unit of the quantity of electricity is *Coulomb. One Coulomb is the quantity of electricity when one ampere current flows through a conductor for one second. One coulomb is given the symbol C.*

If I ampere current flows for t seconds then the quantity of electricity passed is

$$Q = I \times t \text{ coulombs} \tag{14.2}$$

Now if m is the mass in gram of substance liberated at an electrode by passing Q coulomb of electricity, according to Faraday' first law

$$m \propto I \times t$$

where I is the current in Ampere (A) and t is the time (in second) during which current was passed.

Or
$$m = z \times I \times t \tag{14.3}$$

where z is a constant of proportionality, and is known as the *electrochemical equivalent* of the substance. If $I = 1$ A and $t = 1$ second then, $m = z$. Thus,

The electrochemical equivalent is the amount of substance liberated when 1 A current is passed through the electrolyte for 1 second or when one Coulomb of electricity is passed.

Second Law of Electrolysis: *When the same quantity of electricity is passed through different electrolyte solutions of different substances, 'equivalent masses' of the elements are liberated at the electrodes.*

The meaning of the term 'equivalent masses' as used by Faraday needs explanation in the context of present ideas and is described in *Section 14.6.*

These laws have been found to hold under all conditions, provided the current is carried entirely by the ions.

14.5.1 Verification of the First Law of Faraday

Faraday's first law may be verified by measuring the quantity of electricity flowing through an electrical circuit. The apparatus used for the purpose is known as a *voltameter*, or better a *coulometer* (Figure 14.1) because the same apparatus can be used to measure the quantity of electricity passed. In this apparatus the amount of a metal deposited on a clean electrode by passing a known current for a definite time through a solution of a salt of the metal is determined. If $AgNO_3$ solution is used as the electrolyte metallic Ag will be deposited on the cathode, generally a platinum basin containing the silver nitrate solution. The deposit is washed with water, dried and weighed. The mass of the metal deposited can be accurately determined by weighing the electrode before and after passage of the current. If a current I ampere flows for t seconds, the quantity of electricity passed is $I \times t = Q$ coulombs. The mass of metal deposited on passing different quantities of electricity can be determined. The results show that the mass of metal deposited is proportional to Q, the quantity of electricity passed.

The same set up can be used to determine the quantity of electricity Q by using equation (14.2).

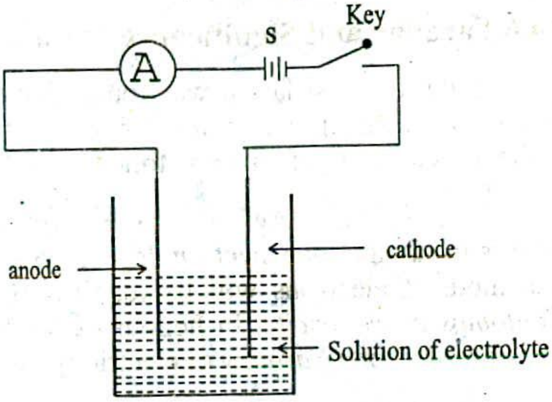


Figure 14.1 Coulometer

14.5.2 Verification of the Second Law of Faraday

The second law can be verified by using solutions of HCl, $AgNO_3$ and $CuSO_4$ in an apparatus as shown in Figure 14.2 which consists of three coulometers arranged in series. In all cases the cathode used is of platinum (an inert metal). The same amount of current is passed for a definite time, and the amount of positive ions liberated at the cathode in each coulometer is determined. It is found that the amount discharged is in the proportion of half mole of hydrogen: one mole of silver: half mole of copper, i.e. to 1 : 107.88 : 31.78 (which were regarded as their respective *equivalent masses*). This verifies the second law. The discharge reactions are

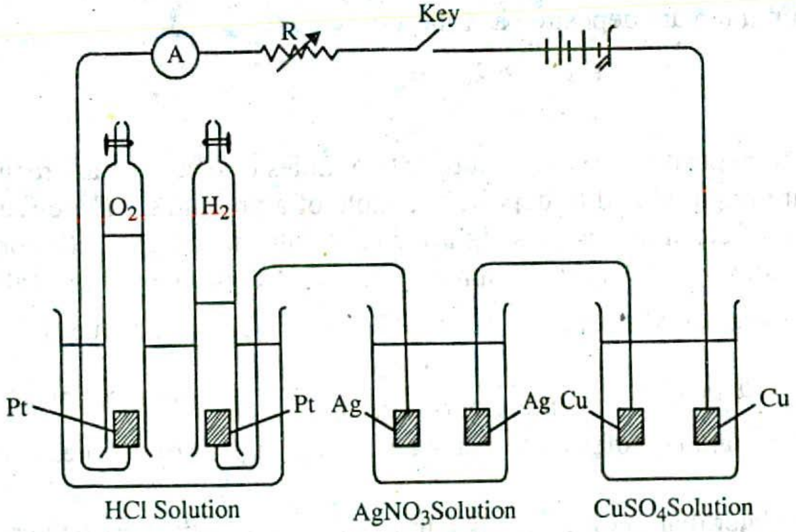


Figure 14.2 Three coulometers in series

$$H^+ + e = \tfrac{1}{2}H_2; \quad Ag^+ + e = Ag; \quad \tfrac{1}{2}Cu^{2+} + e = \tfrac{1}{2}Cu$$

14.6 Faraday and Significance of the Faraday's Laws

Using the first law it was found that the quantity of electricity required to deposit one mole of silver, was 96,500 Coulombs. Now one ion of silver is deposited at the cathode as an atom of silver as follows:

$$Ag^+ + e = Ag$$

That is to say that one electron deposits one atom of silver. To deposit one mole of silver one mole of electrons will be required. Hence *one mole of electrons carries 96,500 Coulombs of electricity*. In honour of Michael Faraday 96,500 Coulombs of electricity was named as one *Faraday* of electricity. So we write

$$1\,F = 96{,}500 \text{ Coulombs} = 96{,}500\,C \qquad (C \text{ stands for Coulomb})$$

and we say that to deposit one mole of silver $1F$ of electricity are required.

Now according to the First Law of Faraday $1F$ will deposit one mole of silver, $2\,F$ will deposit 2 moles of Ag and $3\,F$ will deposit 3 moles of silver.

Since one mole of electrons carry 96,500 Coulombs of electricity the charge carried by one electron = $\dfrac{96{,}500}{6.02\times10^{23}}\,C = 1.60 \times 10^{-19}\,C$

Copper and aluminum are deposited as follows:

$$Cu^{2+} + 2e = Cu$$
$$Al^{3+} + 3e = Al$$

It follows that to deposit one mole of copper two moles of electrons are required, i.e. $2\,F$ of electricity are required and to deposit one mole of aluminium $3\,F$ are required. When 96,500 C or $1\,F$ of electricity is passed through separate electrolytic cells containing Ag^+, Cu^{2+} and Al^{3+} ions respectively the amount of metal deposited at the cathodes in the different cells were found to be Ag, 1 mol; Cu, $\frac{1}{2}$ mol; Al, $\frac{1}{3}$ mol, i.e. in each case the amount of metal deposited = $\dfrac{1.0 \text{ mol}}{\text{number of charges on the ion}}$. As mentioned earlier these amounts are what Faraday referred to as the *equivalent masses* of the metals in the second law.

We will see later that to discharge one mole of oxygen at the anode the reaction is

$$4\,OH^- = 2\,H_2O + O_2 + 4e$$

and $4F$ of electricity will be required.

The Second Law of Faraday may now be stated as follows:

The number of Faradays required to liberate one mole of a metal or discharge one mole of a gas is equal to the number of electrons showed in a balanced equation for the electrode reaction.

Example 14.1: 2.0 ampere current is passed through a *Ag* coulometer for 1 hour 10 minute. Calculate the mass of *Ag* deposited in the coulometer. (R.A.M. of Ag = 107.88)

Solution: Time = $(60 + 10) \times 60$ seconds = 4200 seconds

Electricity passed = $2.0 \times 4200 = 8400\ C$

$$= \frac{8400}{96500} F = 0.087\ F$$

Ag is deposited as shown: $Ag^{+} + e = Ag$

i.e. One *F* deposits one mole of *Ag*

Hence moles of *Ag* deposited = 0.087

Mass of *Ag* deposited = $0.087 \times 107.88\ g$

$= 9.39\ g$

Example 14.2: Calculate the time required to discharge 200 cm^3 of oxygen (measured at r.t.p.) by electrolysing dilute sulphuric acid solution with a current of 4 *A*.

Solution: Oxygen is discharged as shown: $4\ OH^{-} = 2H_2O + O_2 + 4e$

It shows that for the discharge of one mole oxygen 4 *F* of electricity will be required.

$$\text{Now } 200\ cm^3 = \frac{200}{24000}\ \text{mol} = 0.008333\ \text{mol}$$

Quantity of electricity required = $0.008333 \times 4\ F = 0.03333\ F = 3217\ C$

$$\text{Hence the time required} = \frac{3217}{4} = 804 \text{ seconds}$$

14.7 The Conductance of Electrolytic Solutions

The power of conducting electricity by any conductor is described in terms of its conductivity or conductance. Conductance is reciprocal of resistance. If the electrical resistance of a conductor is measured the conductance may be calculated as

$$\text{Conductance} = \frac{1}{\text{Resistance}}$$

Resistance of an electrical conductor may be measured by using Ohm's law written as:

$$R = \frac{E}{I} \tag{14.4}$$

where *R* is the resistance measured in ohms(Ω), *I* is the current in ampere and *E* is the potential difference (volts) between the two ends. This law can be applied in case of solutions except at very high voltages or with very high frequency alternating current.

In order to be able to compare the resistances of different substances the term *specific resistance* has been introduced. The resistance, R, of a conductor is directly proportional to its length, l, and inversely proportional to its area of cross-section, a ; *i.e.*,

$$R \propto \frac{l}{a}$$

Or

$$R = \rho \times \frac{l}{a} \qquad (14.5)$$

where ρ (rho) is a constant for the conducting material and is called its *specific resistance or resistivity*. When $l = 1$ cm and $a = 1$ sq cm, $R = \rho$. The specific resistance is then defined as follows:

> *The specific resistance of a substance is the resistance in ohms between the opposite faces of a cube of the material having an edge one centimeter long.*

The unit of specific resistance can be found from equation (14.5)

$$\rho = \frac{R \times a}{l} = \frac{ohm \times cm^2}{cm} = ohm - cm \quad (\Omega - cm)$$

The reciprocal of resistance is called *conductance*, Λ (lambda).

$$\Lambda = \frac{1}{R} = \frac{1}{ohm} = ohm^{-1} \quad (\Omega^{-1}) \qquad (14.6)$$

The reciprocal of specific resistance is known as the *specific conductance*, κ (kappa). By definition

$$specific\ conductance\ (\kappa) = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a} \qquad (14.7)$$

The unit of specific conductance can be derived as follows:

$$specific\ conductance\ (\kappa) = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a} = \frac{1}{ohm} \times \frac{cm}{cm^2} = ohm^{-1} cm^{-1} \qquad (14.7a)$$

The specific conductance of a solution is dependent on its concentration. In order to compare the conductance of different electrolytic solutions, molar conductance (Λ_m) is used. The molar conductance is defined as,

> *"The conductance of all the ions produced when 1 mole of an electrolyte is dissociated into its ions in a volume V mL."*

This is obtained by multiplying *specific conductance* (κ) by the volume V in *mL* that contains 1 mole of the electrolyte. In other words,

$$\Lambda_m = \kappa \times V \qquad (14.8)$$

where V is the volume of the solution in *mL* containing 1 mole of the electrolyte.

The unit of Λ_m may be derived as follows:

$$\Lambda_m = \kappa \times V$$

$$= \frac{1}{R} \times \frac{l}{a} \times V \tag{14.9}$$

$$= \frac{1}{\text{ohm}} \times \frac{cm}{cm^2} \times \frac{cm^3}{mol}$$

The unit of Λ_m is then $ohm^{-1} cm^2 mol^{-1}$

Example 14.3: A metal rod of length 3.2 cm and area of cross-section 0.45 sq. cm offers a resistance of 1.8 ohms. Calculate its specific conductance.

Solution: Using equation (14.6) specific conductance $\kappa = \frac{1}{1.8} \times \frac{3.2}{0.45}$

$$= 8.0\ ohm^{-1}\ cm^{-1}$$

Example 14.4: An electrolyte solution of concentration 0.1 $mol\ L^{-1}$ has a specific conductance of 0.01289 $ohm^{-1}\ cm^{-1}$. Calculate its molar conductance.

Solution: The volume in mL (V) containing one mol of the electrolyte

$$= \frac{1000}{0.1} = 10000\ mL$$

The molar conductance = $0.01289 \times 10000 = 128.9\ ohm^{-1}\ cm^2\ mol^{-1}$

14.8 Experimental Determination of Conductance

The basic principle of the experimental determination of electrolytic conductance is that of the *Wheatstone's bridge*. A simplified circuit diagram of a conductance bridge is shown in Figure 14.3. This conductance bridge was originally devised by Kohlrausch, and is known as Kohlrausch's conductance bridge. For measuring conductance of solutions direct current cannot be used because electrolysis will take place and polarisation of the electrodes occurs; further complication will be caused by evolution of gases in many cases. Also secondary reactions at the electrodes will spoil the experiments. This difficulty has been eliminated by use of high frequency alternating current from a small induction coil called a 'buzzer' or better from an oscillator. The *a-c* source generates usually 1-3 kilo cycles/sec. Due to rapid change of polarity at the electrodes polarisation is reduced considerably and electrolysis is stopped. The galvanometer in the Wheatstone's bridge circuit is generally replaced by a small sensitive telephone.

a-c current is generated from the 'buzzer' by a storage battery. Two wires connect the *a-c* source to the two ends of the meter bridge at M M. In the gap R is placed a variable decade resistance. M, M and M' are thick metal plates. The solution is placed in a special conductance cell, C, which is connected to the other gap in the bridge between M and M'. The detector, in this case the telephone, is connected to M' and a sliding jockey, S, that connects to the bridge wire AB. A scale, usually one metre long and graduated in millimeters, runs along the wire. The jockey, S, can be moved along the wire so that each position of the jockey, represents a. definite resistance in the wire.

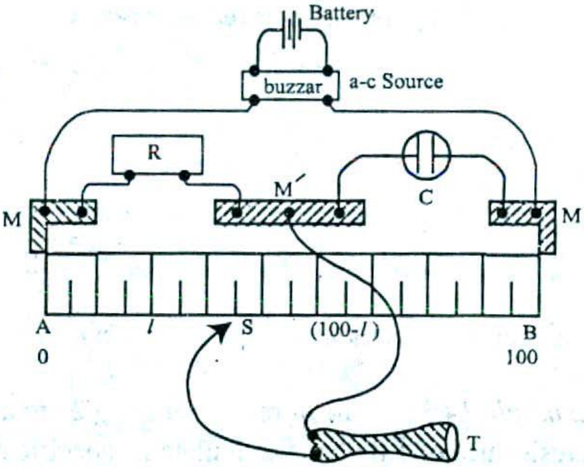


Figure 14.3 Schematic diagram of Wheatstone bridge

When the circuit is completed a buzzing sound is heard in the telephone. A suitable resistance (R) is placed in the gap, R. The sliding contact is then moved along the wire until there is no sound in the phone or the sound is minimum. This is the null point. The resistance is usually so chosen that the null point is at about the middle of the scale. If the length of the wire, AB, is 100 cm and null point is at a distance *l* cm from the end A, then the principle of the Wheatstone's bridge gives

$$\frac{\text{R}}{\text{Cell resistance}} = \frac{l}{(100-l)} \tag{14.10}$$

or

$$\text{Cell resistance} = \text{R}\left(\frac{100-l}{l}\right)$$

or

$$\text{Cell conductance} = \frac{l}{R(100-l)} \tag{14.11}$$

Since l and R are known the conductance of the solution in the cell is at once calculated.

This simple bridge can give only moderately good values of conductance. It is very difficult and sometimes impossible to get a sharp minimum in the bridge. Use of a small variable parallel plate condenser, like one used in a radio for tuning, connected parallel to the conductivity cell improves the minimum, but even then there are other sources of error.

Many good and sophisticated bridges are commercially available. The principle of all these bridges is the same as above but the *a-c* current is generated by an electronic oscillator. For better sensitivity the current is amplified before being fed to the detector.

The detector generally is a cathode-ray tube (magic eye as in a radio) or in more expensive and sensitive instruments it is a cathode ray oscilloscope. Precise and reliable conductance values can be obtained from such improved instruments only.

14.9 Conductance Cell: Cell Constant

A conductance cell is a devise to measure the conductance of electrolytic solutions. Different forms of cells are in use for conductance measurement. A cell which is commonly used is shown in Figure 14.4. The container is a glass vessel, *A*, which carries two thick platinised platinum (fine particles of platinum, black in colour, deposited on the platinum foil electrolytically) foils, *PP*, securely fixed so that their distances are not altered. Two metallic wires, *BB*, sealed to the platinum foils and protected by glass tubes serve as the leads for connecting to the measuring bridge. Several other forms of cells are shown in Figure 14.5.

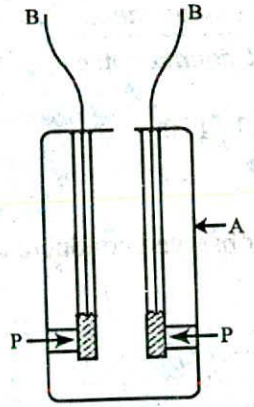


Figure 14.4 A conductance cell

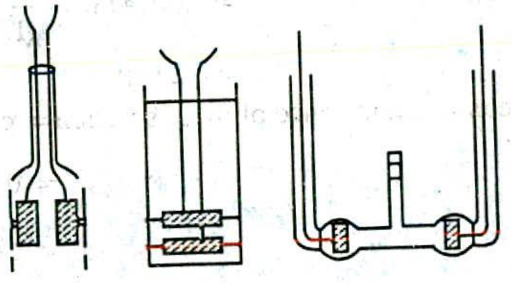


Figure 14.5 Different types of conductance cells

It is known from equation (14.5) that the resistance of a conductor is given by

$$R = \rho \times \frac{l}{a}$$

In the case of conductance cell *l* is the distance between the two electrodes and *a* is the area of cross-section of the electrodes, as the resistance of the column of solution between the two electrodes is measured. For a particular cell *l/a*, known as *cell constant,* is a constant. As the dimension of the electrodes and the distance between them can hardly be measured accurately the usual practice is to determine the cell constant by measuring the conductance of a solution whose specific conductance is accurately known at a particular temperature. Standard solutions of *KCl* are used for the purpose. The specific conductance of any solution may then be obtained from the equation (14.7).

$$\textit{Specific conductance} = \textit{Observed conductance} \times \textit{cell constant} \qquad (14.12)$$

The specific conductance of *KCl* at different concentrations are given in Table 14.2

Table 14.2 Specific conductance of *KCl* solutions at different concentrations at 25°C

Concentration ($mol\ L^{-1}$)	Specific conductance($ohm^{-1}\ cm^{-1}$)
1.0	0.11173
0.1	0.012886
0.01	0.001411

Example 14.5: A conductivity cell has a resistance of 170 ohms when filled with 0.01 $mol\ L^{-1}$ solution of *KCl* at 25°C. The specific conductance of this solution is 0.001411 $ohm^{-1}\ cm^{-1}$. The same cell when filled with *NaCl* solution of concentration 0.01 $mol\ L^{-1}$ has a resistance of 235 *ohm*. Calculate the specific conductance and molar conductance of the *NaCl* solution.

Solution: From equation (14.12) cell constant $= \dfrac{specific\ conductance}{observed\ conductance}$

$$= 0.001411 \times \frac{1}{(1/170)} = 0.001411 \times 170$$

$$= 0.24\ cm^{-1}$$

Specific conductance of *NaCl* solution = cell constant × observed conductance

$$= 0.24 \times \frac{1}{235}$$

$$= 0.001021\quad ohm^{-1}\ cm^{-1}$$

Volume (V) of solution containing one mol of *NaCl* $= \dfrac{1000}{0.01} = 100000\ mL$

From equation (14.8) molar conductance = specific conductance × V

$$= 0.001021 \times 100000$$

$$= 102.1\ ohm^{-1}\ cm^{2}\ mol^{-1}$$

14.10 Conductivity Water

For conductance measurements it is necessary to use very pure water because the impurities, if present, might contribute to the total conductance, thereby giving incorrect results. Water for conductance measurements, known as *conductivity water*, can be obtained by three distillations of ordinary water with addition of small amounts of potassium permanganate in an all glass (pyrex) distillation set. Purer water can be obtained by using tin-plated copper condensers. Alternatively, the water may be passed through mixed bed ion-exchange resins when de-ionized water can be obtained. For most purposes the water should not have a specific conductance more than $2 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$ at 25°C.

14.11 Conductance and Electrolyte Concentration

It has been mentioned that the specific conductance of solutions depends on the concentration of the electrolyte. A look at Table 14.1 will reveal it clearly. As the current is carried by ions the specific conductance will depend on the actual number of ions per unit volume of the solution. Hence the specific conductance progressively decreases with increasing dilution (i.e. decreasing concentration). However, the molar conductance, Λ_m, increases with dilution and tends to attain a limiting constant value for strong electrolytes; but for weak electrolytes, like ethanoic acid, NH_4OH etc., the molar conductance rises rapidly at low concentrations. The behaviour of both strong and weak electrolytes are shown in Figure 14.6

The plots for Λ_m *vs* $\sqrt{molarity}$ for strong electrolytes like KCl, Na_2SO_4, CH_3COONa follow almost a linear relation at low concentration and the straight lines can be extrapolated to zero concentration to give Λ^0_m, the molar conductance at infinite dilution*: But the curve for ethanoic acid shows a rapid upward trend for $\sqrt{c}$ values approximately below 0.05. Extrapolation of such a curve to zero concentration is neither feasible nor at all reliable.

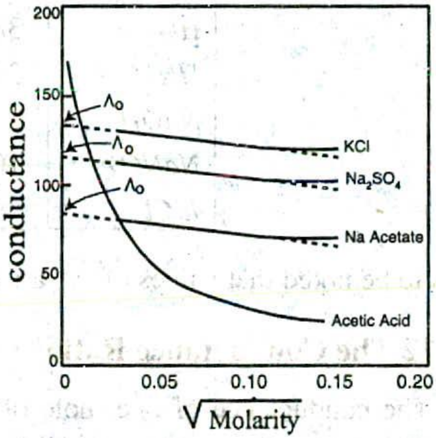


Figure 14.6 Molar conductance *vs* square root of concentration

Table 14.3 Molar conductance (*ohm^{-1} cm^2 mol^{-1}*) of different electrolytes in aqueous solutions at 25°C

C *mol L^{-1}*	*NaCl*	*KCl*	*HCl*	*$AgNO_3$*	*HAc*
0.0000	126.45	149.86	426.16	133.4	(390.7)
0.0005	124.50	147.81	422.74	131.4	67.7
0.001	123.74	146.95	421.36	130.5	49.2
0.01	118.51	141.27	412.00	124.8	16.3
0.10	106.74	128.96	391.32	109.1	5.2

---

* *At very tow concentrations the line shows an upward trend even in case of strong electrolytes like KCl, NaCl etc.*

The measurement of Λ_m at very low concentrations serves as an excellent method for distinguishing between strong and weak electrolytes. Some data on molar conductance are given in Tables 14.3 and 14.4.

Table 14.4 Molar conductance (ohm^{-1} cm^2 mol^{-1}) at infinite dilution at 18°C

Electrolyte	Λ^0	Electrolyte	Λ^0
$LiCl$	98.9	CH_3COOAg	88.0
KCl	129.9	KNO_3	126.3
$NaCl$	108.9	$KClO_3$	119.4
HCl	381.0	$AgClO_3$	109.0
HNO_3	377.5	KOH	238.0
$NaOH$	216.5	$LiNO_3$	95.2
$NaNO_3$	105.3	CH_3COONa	77.0
$LiCl$	98.8		

It is to be noted that values of Λ_m^0 are different at different temperatures.

14.12 The Conductance Ratio

The conductance of one mole of a particular electrolyte in solution will depend on (a) the number of ions and (b) the speeds of the ions. The difference in the molarconductance of different electrolytes may be attributed to difference in speeds (*see Section 14.13*). The variation of molar conductance of a given electrolyte with concentration was explained by Arrhenius (*Section 14.6*) by assuming that the extent of dissociation of the electrolyte increases with increasing dilution. At infinite dilution the dissociation would be complete and the value of Λ_c would not change with further dilution, i.e., the molar conductance would reach its limiting value, Λ^o. Since the molar conductance at any concentration, Λ_c, is proportional to the number of ions, the extent of dissociation at the concentration, c, would be given by

$$\alpha = \frac{\Lambda_c}{\Lambda^0} \qquad (14.13)$$

Arrhenius named this quantity the degree of dissociation. As will be seen in *Section 14.11*, all strong electrolytes are now supposed to be completely dissociated into ions in solution, and the term has little significance except in the case of weak electrolytes which are regarded as incompletely dissociated. The ratio $\frac{\Lambda_c}{\Lambda^0}$ is now given the non-committal term, *conductance ratio*.

14.13 Debye-Hückel- Onsager Theory

Based on his analysis of the data available and his own experimental results the following empirical equation relating molar conductance (he was using equivalent conductance) with concentration was put forward by Kohlrausch

$$\Lambda = \Lambda^o - A\sqrt{C} \tag{14.14}$$

where A is a constant. The constant A is characteristic of the electrolyte. The first satisfactory theoretical interpretation of the equation, however, was given in 1920 by Debye, Huckel and Onsager, and the constant A in Kohlrausch's equation became meaningful.

Development of the study of crystals by X-rays and the electronic theory of valency led to the view that when a salt, strong acid or strong base is dissolved in water these are completely ionized. In the Debye-Huckel-Onsager theory this is accepted as a fact and the increase of molar conductance with dilution is explained in terms of decreasing inter-ionic attraction at low concentration.

Debye-Hückel-Onsager theory is based on the following assumptions:

- Strong electrolytes are completely dissociated into ions
- Due to Coulombic forces between the charges of the ions, they do not behave like molecules in their transport and thermodynamic properties
- Since the solution as a whole is neutral, the total number of positive charges must be equal to the total number of negative charges.
- A given ion will have more ions of the opposite sign close to it than ions of the same sign. This *cluster of ions* is called the *ionic atmosphere*.

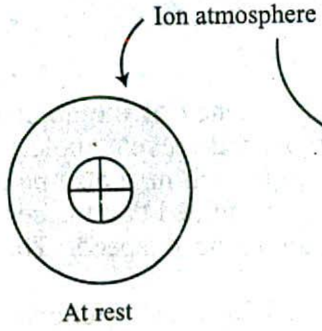


Figure14.7 Ion atmosphere

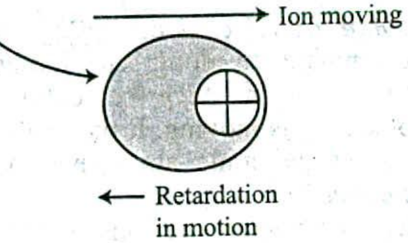


Figure 14.8 Asymmetry effect

When an electrical potential is applied to an electrolytic solution, two effects produced by the *ionic atmosphere* prevent the ions to move at the expected speed and hence conducting the amount of current. These effects are:

(i) Relaxation effect (sometimes known as asymmetry effect):

In an electrolytic solution, each ion is surrounded by an atmosphere of counter-ions, e.g., ions having opposite charge (*ionic atmosphere*). In other words, cations are surrounded by an atmosphere of anions and vice versa. In the absence of an external field the ion, along with its *surrounding ionic atmosphere,* remains fairly steady and the ionic atmosphere remain symmetrial around the central ion. When such a system is subjected to an external electric field, the central ion and its ionic atmosphere moves toward the oppositely charged electrode. As the central ion starts moving out of the *ionic atmosphere* a new ionic atmosphere of opposite charge starts building around it. The old ionic atmosphere will eventually die out. The destruction of an ionic atmosphere and the completion of the formation of a new ionic atmosphere do not take place all at once. There is a time lag between these two processes. This time lag is termed as *relaxation time*. During this relaxation time the old ionic atmosphere pulls the moving ion backward and thus retards its motion.

The *relaxation effect*, also called the *asymmetry effect,* may be looked upon from a different perspective. Once the external field is applied, the central ion starts moving toward the electrode of opposite charge and more of the ionic atmosphere is left behind than is present on the front side. These excess ions of the ionic atmosphere which are left behind will tend to retard the speed of the moving ion due to electrostatic force. Thus the effect arises because of the asymmetry of the ionic atmosphere, and hence the effect is called *asymmetry effect*. An approximate representation of the above statements is given in Figure 14.8.

The arrow at the top of the 'ion atmosphere' represents the velocity with which the cation would have moved to the cathode if no retarding force was in operation. The small arrow below the ion atmosphere shows the retarding force. Since in a solution of one mole of the electrolyte the number of ions is constant this retardation of the velocity of the ions brings about an overall decrease in molar conductance from its ideal value that the solution would have in absence of any other force.

(ii) Electrophoretic effect:

The *electrophoretic effect* is caused by the tendency of the applied electric field to move the ionic atmosphere along with the associated solvent molecules in a direction opposite to the direction in which the central ion (which may also be accompanied by a few solvent molecules) is moving. It may well be imagined that the central ion is moving against the flow of the ionic atmosphere with reduced speed. This effect is called *electrophoretic effect.*

Finally, the migration of the ions is opposed by usual frictional resistance of the medium which is again dependent on the dielectric constant of the medium, the radius of the ionic atmosphere and the viscosity of the medium.

At infinite dilution, the asymmetry and electrophoretic effects are practically zero, and the speed of the ions, and hence the molar conductivity is determined by frictional force of the medium only.

On the basis of these arguments Debye and Hückel were able to derive an expression to explain the variation of conductance with concentration of the electrolyte. This can be written in the modern form as below:

$$\Lambda_m^c = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{C} \qquad (14.15)$$

Λ_m^c = molar conductance of the electrolyte solution of concentration $C\ mol\ L^{-1}$

Λ_m^0 = molar conductance of the electrolyte solution at infinite dilution

A and B = constant terms for a particular solvent at a given temperature

On increasing the dilution the average distance between ions increases and, therefore, the retarding force decreases, and there is an increase in Λ_m with increase in dilution. The above explanation, which is only a fragmentary reflection of a more detailed picture, leads to a relation between molar conductance and concentration of the same form as Kohlrausch's equation. Debye, Huckel and Onsager were able to calculate the constant A and B for many electrolytes in dilute solution. The calculated values were found to be in agreement with the values found from the slopes of the experimental data plotted as Λ_m vs $\sqrt{C}$.

The theory which explains many other facts, however, fails when applied to solutions of moderate or higher concentration, i.e., 0.1 to 1 $mol\ L^{-1}$ and above. Although no satisfactory theoretical treatment for such solutions is still available, mention may be made of the concept of the formation of *ion- pairs or ion triplets,* primarily by Fuoss, Bjerrum and others. Because of the proximity of the ions at high concentrations there may be specific attraction between the oppositely charged ions, so that two oppositely charged ions in an ion -pair will virtually behave like an undissociated molecule so far as conductance is concerned. The ion-pairs cannot be regarded as molecules as these can exchange partners. The concept of ion-pair is of importance particularly in solutions of low dielectric constant.

14.14 Independent Migration of Ions: Kohlrausch's Law

Kohlrausch examined the values of Λ_m^0 of a number of strong electrolytes with common anions or cations and found some regularity in the Λ_m^0 values of various electrolytes. He observed that when the electrolytes were considered in pairs having one common ion the difference between the Λ_m^0 values were constant (Table 14.5).

Table 14.5 Differences in values of Λ_m^0 for several pairs of electrolytes with a common ion

Electrolyte	Λ_m^0 at 298 K $\Omega^{-1}\ cm^2 mol^{-1}$	Difference	Electrolyte	Λ_m^0 at 298 K $\Omega^{-1}\ cm^2 mol^{-1}$	Difference
KBr $NaBr$	151.92 128.51	23.41	KBr KCl	151.92 149.86	2.06
KCl $NaCl$	149.86 126.45	23.41	$NaBr$ $NaCl$	128.51 126.45	2.06
KNO_3 $NaNO_3$	144.96 121.55	23.41	$LiBr$ $LiCl$	117.09 115.03	2.06

These observations led Kohlrausch (1875) to state that *the molar conductance at infinite dilution is different for different electrolytes and is equal to the sum of the conductanc of the constituent ions of the electrolytes.* This is known as the *Kohlrausch's law of independent ionic migration.* The law may be expressed in the form

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0 \tag{14.16}$$

where λ_+^0 and λ_-^0 are called the ion conductance of the cation and anion respectively. The above equation means that each ion of an electrolyte contributes independently to the value of Λ_m^0 at infinite dilution. For example, the molar conductance of KCl at infinite dilution is 149.86 $\Omega^{-1} cm^2 mol^{-1}$. The ion conductances of K^+ and Cl^- are 73.50 and 76.30 $\Omega^{-1} cm^2 mol^{-1}$. According to *Kohlrausch's law of independent ionic migration,*

$$\begin{aligned}\Lambda_{m(KCl)}^0 &= \lambda_{K^+}^0 + \lambda_{Cl^-}^0 \\ &= 73.50 + 76.30\ \Omega^{-1} cm^2\ mol^{-1} \\ &= 149.80\ \Omega^{-1} cm^2\ mol^{-1}\end{aligned}$$

This is in agreement with the value measured directly. The *Kohlrausch's law of independent ionic migration* is useful for calculation of Λ^0 for weak electrolytes for which Λ_m^0 cannot be ascertained from the plot of Λ_m vs $\sqrt{C}$ as shown in Figure 14.6.

Table 14.6 Ion conductance at 25°C

Cation	λ_+^0 ($\Omega^{-1} cm^2\ mol^{-1}$)	Anion	λ_-^0 ($\Omega^{-1} cm^2 mol^{-1}$)
H^+	350.0	OH^-	198.0
Li^+	38.7	Cl^-	76.3
Na^+	50.1	Br^-	78.4
K^+	73.5	I^-	76.8
Rb^+	77.8	NO_3^-	71.4
Cs^+	77.3	ClO_4^-	68.0
NH_4^+	73.4	SO_4^{2-}	160.0
Ag^+	61.9	CO_3^{2-}	140.0
Ba^{2+}	127.2	$C_2O_4^{2-}$	48.0
Fe^{3+}	204.0	CH_3COO^-	40.9

The computation is done by addition and subtraction of Λ_o values for different strong electrolytes.

Example 14.6: The molar conductances at 25°C of HCl, $NaCl$ and CH_3COONa are 426.1, 126.4 and 91.00 $\Omega^{-1} cm^2 mol^{-1}$ respectively at infinite dilution. Calculate the molar conductance of CH_3COOH at infinite dilution.

Solution: From Kohlrausch's law

$$\Lambda^0_{HCl} = \lambda^0_{H^+} + \lambda^0_{Cl^-} = 426.1\ \Omega^{-1}\,cm^2mol^{-1} \qquad \text{(i)}$$

$$\Lambda^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-} = 126.4\ \Omega^{-1}\,cm^2mol^{-1} \qquad \text{(ii)}$$

and

$$\Lambda^0_{CH_3COONa} = \lambda^0_{CH_3COO^-} + \lambda^0_{Na^+} = 91.00\ \Omega^{-1}\,cm^2mol^{-1} \qquad \text{(iii)}$$

Adding equations (ii) and (iii) and subtracting equation (i) from the sum we obtain

$$\lambda^0_{CH_3COO^-} + \lambda^0_{H^+} = 390.70\ \Omega^{-1}\,cm^2mol^{-1}$$

Or,

$$\Lambda^0_{CH_3COOH} = 390.70\ \Omega^{-1}\,cm^2mol^{-1}$$

Example 14.7: Calculate the molar conductance at infinite dilution of NH_4OH, given that the molar conductance of NH_4Cl, $NaCl$ and $NaOH$ at infinite dilution at 25°C are 149.7, 126.4 and 248.1 $\Omega^{-1}\,cm^2mol^{-1}$ respectively.

Solution: We can write,

$$\Lambda^0_{NH_4OH} = \lambda^0_{NH_4^+} + \lambda^0_{OH^-} = \lambda^0_{NH_4^+} + \lambda^0_{Cl^-} + \lambda^0_{Na^+} + \lambda^0_{OH^-} - \lambda^0_{Na^+} - \lambda^0_{Cl}$$

$$= \Lambda^0_{NH_4Cl} + \Lambda^0_{NaOH} - \Lambda^0_{NaCl}$$

$$= 149.7 + 248.1 - 126.4 = 271.4\ \Omega^{-1}\,cm^2mol^{-1}$$

14.15 Absolute Velocity of Ions: Ionic Mobility

The difference in the ion conductances may be traced to the difference in the speeds with which the ions move under a given potential gradient. A direct measurement of the speeds with which ions move, i.e., their absolute velocities were first made by Oliver Lodge. A simple apparatus of the type as shown in Figure 14.9 was used. In the tube was placed a gel into which was incorporated some indicating material. For example, in measuring the speed of hydrogen ion the anode and the cathode vessels are filled with dilute sulphuric acid and sodium sulphate. The tube is filled with a gel of agar-agar to which phenolphthalein and a trace amount of alkali was incorporated so as to give a pink colour to the gel. On passing electric current through the electrodes the hydrogen ion moves towards the cathode. The rate of movement is followed by noting the rate of disappearance of the colour in the gel due to neutralization of alkali by the hydrogen ions.

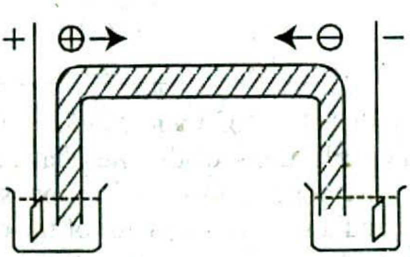


Figure 14.9 Apparatus used by Lodge to measure the absolute velocity of ions

The success of the method depends on producing sharp boundaries and observing the movements of the boundaries accurately. However, the speeds will depend on the potential gradient across the electrodes. In order to compare the speeds of different ions a term *ionic mobility* has been introduced. The *ionic mobility* is defined as

"The velocity of an ion in cm per second when it moves under unit potential gradient", i.e., when the potential between two electrodes placed 1 cm apart is 1 volt.

The ionic mobility, u, is related to ion conductance λ by the expressions

$$\lambda_a \propto u_a \text{ or } \lambda_a = ku_a \tag{14.17}$$

and

$$\lambda_c \propto u_c \text{ or } \lambda_c = ku_c \tag{14.18}$$

In equations (14.17) and (14.18), λ_a *and* λ_c are the ion conductance of anion and cation respectively and k is a constant of proportionality. The value of the constant k has been shown to be equal to one Faraday.

If we consider the ion conductance at infinite dilutions it can be shown that

$$\lambda_a^0 + \lambda_c^0 = k(u_a + u_c) \tag{14.19}$$

These relations enable one to calculate the ionic mobility from the values of ion conductance.

Example 14.8: The ion conductance of H^+ and Cl^- ions, in $ohm^{-1}\ cm^2\ mol^{-1}$, are respectively 350 and 76.3. Calculate their ionic mobility. ($1F = 96500C$)

Solution: Ionic mobility of $H^+ = \dfrac{350}{96500} = 36.27 \times 10^{-4}\ \text{cm}^2\ \text{sec}^{-1}\ \text{V}^{-1}$

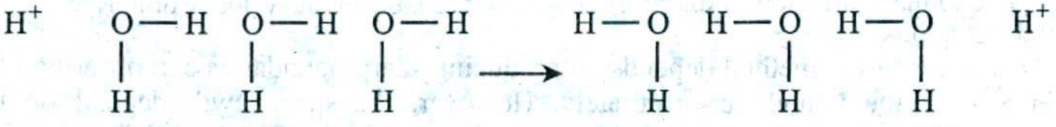
Ionic mobility of $Cl^- = \dfrac{76.3}{96500} = 7.91 \times 10^{-4}\ \text{cm}^2\ \text{sec}^{-1}\ \text{V}^{-1}$

Some values of ionic mobility are given in Table 14.7.

Table 14.7 Ionic mobility of some ions at 25°C ***($cm^2\ sec^{-1}\ V^{-1}$)***

Ion	$u_c \times 10^4$	Ion	$u_a \times 10^4$
H^+	36.30	OH^-	20.50
Li^+	4.01	Cl^-	7.91
Na^+	5.19	I^-	7.95
K^+	7.61	NO_3^-	7.40
Ca^{2+}	6.16	SO_4^{2-}	8.27
La^{3+}	7.21		

The high values of ionic mobility for H^+ and OH^- compared to others should be noted. The explanation of this fact has been given in terms of the Grotthus's mechanism of electrolytic conductance. It is supposed that H^+ or OH^- approach a group of water molecules and a series of transfer of the charge between the water molecules in the group takes place. As a result of this the ion is transported through the solution. This is illustrated below for H^+.



$$H^+\ \ O{-}H\ \ O{-}H\ \ O{-}H \longrightarrow H{-}O\ \ H{-}O\ \ H{-}O\ \ H^+$$

This explanation is not, however, applicable to other ions.

Another interesting fact is that the heavier members of the alkali metal group have higher mobility. This is explained by the higher degree of hydration of the lighter ions which makes its effective size large.

14.16 Applications of Conductance Measurements

Conductance of electrolytes depends on the number of ions and their speeds. The measurements of conductance of electrolytic solutions have been utilized for determining

(a) the end points of acid-base titrations,
(b) the end points of precipitation titrations,
(c) the solubility of sparingly soluble salts and
(d) the kinetics of reactions.

For conductometric titration experiments a known volume of the solution to be titrated is placed in a beaker and a conductivity cell dipped into it. The conductivity cell is now connected to one end of the Wheatstone's bridge. The other solution is then added to the solution in the beaker in instalments and the conductance measured after each addition. This is continued beyond a sharp change in conductance value. The conductance values are then plotted against the volumes of titre added. In each case the straight line portions of the graph are extrapolated and the point at which the straight lines intersect is taken as the end point of the titration.

(a) *Conductometric titrations involving acids and bases*

(i) Titration of strong acid and strong base:

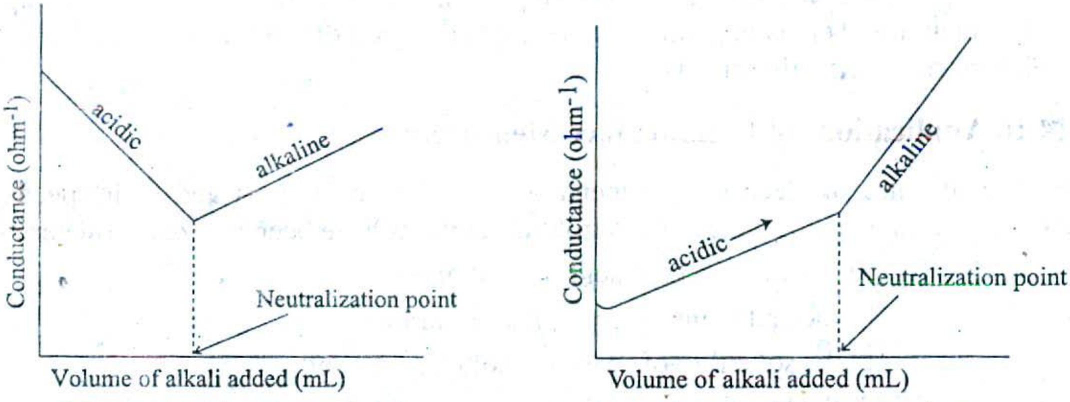
Let us consider the titration of a solution of *HCl* by *NaOH* solution. The net reaction in this neutralization reaction is the production of water from H^+ and OH^-. The neutralization reaction can be written as

$$H^+(aq)+Cl^-(aq)+Na^+(aq)+OH^-(aq) \rightarrow H_2O(l)+Na^+(aq)+Cl^-(aq)$$

If we cancel the common terms from both sides the net ionic reaction becomes

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

In presence of the acid or base all the water will remain practically undissociated. However, H^+ ion of the acid is gradually replaced by Na^+ as *NaOH* is added to the acid solution. Since the ionic conductance of H^+ is much higher than that of Na^+ there will be a decrease of the conductance as the addition of *NaOH* continues. This will go on until all the acid is neutralized. If more *NaOH* is added after the neutralization point, the conductance of the solution in the titration vessel will again increase as the ionic mobility of OH^- is very large (Table 14.7). If the conductance values are graphically plotted against the corresponding volumes of *NaOH* added, a conductometric titration curve is obtained (Figure 14.10(a)). The point of intersection of the two straight lines gives the *end point* of titration. Thus acid-base titration can be carried out conductometrically.



(a) strong acid *vs* strong base

(b) weak acid *vs* strong base

Figure 14.10 Conductometric titration curves

(ii) *Titration of weak acid and strong base:*

Let us consider that ethanoic acid is titrated against $NaOH$. The initial conductance of the acid solution is very low because of low ionization of the weak acid. However, as $NaOH$ is gradually added to the acid solution a salt, CH_3COONa, will be formed which ionizes readily to form Na^+ and CH_3COO^- ions. The ethanoate ions at first tend to suppress further ionization of the acid due to *common ion effect*. But after a while the conductance of the system increases because the conducting power of the completely ionized salt exceeds that of the weak acid. This continues to increase up to the end point, V [Figure 14.10(b)]. Beyond this point as more $NaOH$ is added the conductance rapidly increases due to highly conducting OH^-. Consequently, the linear portion of the conductance curve in the alkaline region is steeper. The end point is the point of intersection of the two lines – one in the acidic region and the other in the alkaline region.

(iii) *Titration of weak acid and weak base:*

For weak acid and weak base the conductance initially rises due to the formation of a salt, say ammonium ethanoate from NH_4OH and CH_3COOH. On further addition of NH_4OH the conductance continually rises till the neutral point is reached. After this the conductance remains almost constant because NH_4OH is a very weak base and contributes only very slightly to conductance. The titration curve for a weak acid – weak base is shown in Figure 14.11. The point of intersection of the two linear portions gives the neutral point. Almost all acid-base titrations can be performed conductometrically.

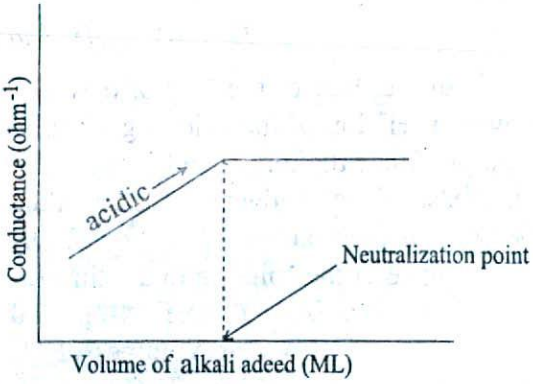


Figure 14.11 Titration of weak acid *vs* weak base

Conductometric titrations have the following advantages over volumetric titration:

(i) No indicators are required and, therefore, coloured solution can be conveniently titrated.

(ii) For weak acid and weak base no suitable indicators are available but conductometric titrations can be conveniently carried out.

(iii) More accurate results are obtained by conductometric titrations because the end-point is determined graphically from a number of measurements and not from a single measurement as in volumetric titration.

(iv) Conductometric titrations can be accurately carried out for very dilute solutions, where indicator colour change is not sharp.

(v) Volumetric titration does not give correct end point for polybasic acids, while conductometric titration can be conveniently used in such cases.

However, it must be kept in mind that in order to minimize the volume change as little as possible the *titre* should be about 10 times stronger than the solution to be titrated. Also, the temperature of the solution should be kept constant during titration.

(c) Conductance titration in precipitation reactions:

In a precipitation reaction there is a net decrease in the number of ions in the solution due to removal of the ions from both the reacting substances. For example, when a solution of $MgSO_4$ is added to a solution of $Ba(OH)_2$ the Ba^{2+} ions and SO_4^{2-} are removed as $BaSO_4$ and Mg^{2+} ions and OH^- are removed as $Mg(OH)_2$ according to the equation:

$$Ba^{2+}(aq) + 2OH^-(aq) + Mg^{2+}(aq) + SO_4^{2-}(aq) = BaSO_4(s) + Mg(OH)_2(s)$$

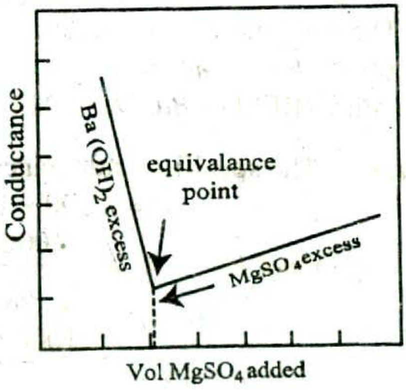


Figure 14.12 Precipitation titration by conductance measurements

Therefore, upon addition of a solution of $MgSO_4$ to $Ba(OH)_2$ solution there is a sharp fall in the conductance and this continues until the equivalence point is reached as shown in Figure 14.12.

However, after the equivalence point is exceeded, the conductance rises due to the contribution of Mg^{2+} and SO_4^{2-} ions from the added $MgSO_4$ solution. The method can be used for quantitative estimation of either Ba^{2+}, Mg^{2+} or SO_4^{2-}. In several other precipitation reactions the same method can be used and no indicators are needed. Conductance titrations can be used for quantitative estimations of cations and anions in a variety of reactions. The principle, in all cases, is the change in the conductance of the reaction system due to addition or removal of some ions.

(d) Determination of solubility of sparingly soluble salts:

Conductance measurement can be used for measurements of solubility of slightly soluble substances like $BaSO_4$, $PbSO_4$, $AgCl$ etc. The method is based on the difference in the conductance of the ions of the salts. For the purpose a saturated solution of the salt is prepared in conductivity water and allowed to stand until almost all the insoluble fraction settles down. The clear solution from the top is taken and its conductance is measured in a conductance cell whose cell constant has been determined earlier. The cell is thoroughly washed and filled with the same conductivity water and the conductance of the water measured in the same cell. The observed conductance is then converted to specific conductance. The conductance of water is then subtracted from the conductance of the solution. The value so obtained is the conductance due to the salt. The molar conductance (Λ_m) of a saturated solution is given by equation (14.8)

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

where κ is the specific conductance and c is the concentration of the solution in $mol\ L^{-1}$. Since the salt is sparingly soluble, the solution is very dilute and Λ_m may be considered to be equal to Λ_m^0 i.e., the molar conductance at infinite dilution. The value of Λ_m^0 for $AgCl$ can be found by applying Kohlrausch's law of independent ionic migration. According to this law, $\Lambda^0_{m(AgCl)} = \lambda^0_{Ag^+} + \lambda^0_{Cl^-}$. Substituting Λ_m^0 in above equation c can be calculated provided κ is known. This will give the value of c in $mol\ L^{-1}$ from which the solubility in $g\ L^{-1}$ may be calculated.

Example 14.9: The specific conductance of a saturated solution of $BaSO_4$ at 25°C is $3.590 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$ and that of the conductivity water used is $0.618 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$. The limiting ion conductance at infinite dilution for Ba^{2+} and SO_4^{2-} ions are 127.2 and 160.0 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. Calculate the solubility of $BaSO_4$ at this temperature (RFM of $BaSO_4$ = 233).

Solution: The specific conductance of the solute,

$$\kappa = 3.590 \times 10^{-6} - 0.618 \times 10^{-6} = 2.972 \times 10^{-6}$$

Solubility in $mol\ L^{-1}$ $\quad c = \dfrac{1000\kappa}{\Lambda_m^0} = \dfrac{1000\kappa}{\lambda_+^0 + \lambda_-^0}$

$$= \frac{1000 \times 2.972 \times 10^{-6}}{287.2} = 1.035 \times 10^{-5}$$

Solubility in $g\ L^{-1}$ $= 1.035 \times 10^{-5} \times (233) = 2.41 \times 10^{-3}$

14.17 Transport Number (or Transference Number)

In an electrolytic solution the current is carried by both cations and anions. In a solution of an electrolyte where the number of ions is fixed or does not vary much, the conductance would be mainly governed by ionic velocities. If u_+ represents the ionic velocity of the cation and u_- that of the anion then the current carried by the cation will be proportional to u_+ and the current carried by anion will be proportional to u_-. The total current carried through the solution will be proportional to $(u_+ + u_-)$.

*The fraction of the current curried by each ionic species is called the **transport number** of that ion*

The transport numbers of anions and cations are given by

$$t_- = \frac{A.u_-}{A.u_+ + A.u_-} = \frac{u_-}{u_+ + u_-} \tag{14.20}$$

and

$$t_+ = \frac{A.u_+}{A.u_- + A.u_+} = \frac{u_+}{u_- + u_+} \tag{14.21}$$

where t_+ and t_- are the transport number of cation and anion respectively and A is the proportionality constant. It is evident that $t_+ + t_- = 1$ since

$$\frac{u_+}{u_- + u_+} + \frac{u_-}{u_+ + u_-} = 1$$

So $$t_+ = 1 - t_-$$

and $$t_- = 1 - t_+$$

Due to the unequal velocities of the cation and the anion there will be a change in the concentration of the ion around the cathode and the anode. To explain this let us consider an arrangement of electrolysis as shown in Figure 14.13. The whole cell is divided into three imaginary compartments by the dotted lines *aa* and *bb*, the left is the anode compartment, the right one is the cathode compartment and between *aa* and *bb* is the middle compartment.

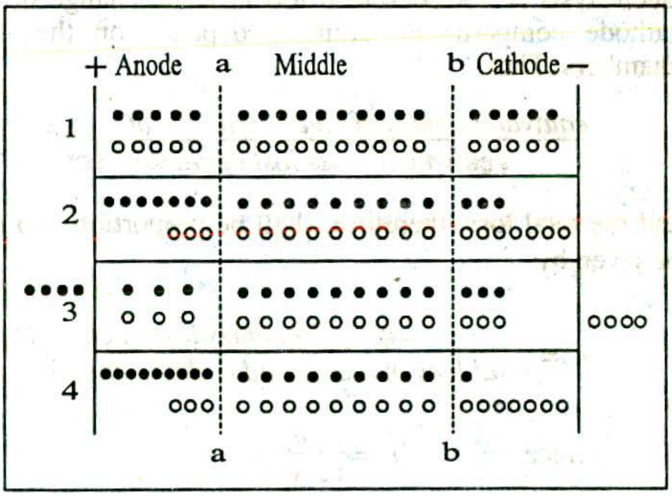


Figure 14.13 Mechanism of ionic transport

Let us assume that before electrolysis starts there are *five* anions (solid circles) and *five* cations (hollow circles) in each of the cathode and anode compartments and *ten* cations and *ten* anions in the middle compartment. The following cases may now be considered:

(I) *There is no electrolysis*

The number of anions and cations are the same in each compartment. This corresponds to the situation in line 1 in the diagram.

(II) *The anions and cations move with the same speed*

On electrolysing for a certain time, equal number of the two ions would have migrated in opposite directions and the system would resemble the line 2 where two ions of each kind have migrated in opposite direction. The number of anions and cations ions in the middle compartment will remain the same since it has lost two ions and has gained two ions. For electrical neutrality four anions from the anode and four cations from the cathode must be discharged. In line 3 is shown the liberation of the ions on the electrodes, the cation on the cathode and anion on the anode. Since the ions are lost from the solution they are shown outside the system. The whole solution has become dilute, but the composition in the middle compartment remains unchanged.

(III) *The anions move at twice the speed of the cations.*

Let us assume that the anionic velocity is twice the velocity of the cation, the system would be represented by the line 4. Two cations move to the cathode chamber while four anions move to the anode chamber. The anode compartment has now nine anions and three cations but the cathode compartment has only one anion and seven cations. On continued electrolysis therefore, the concentrations around cathode and anode would change but the composition in the middle compartment will remain constant if electrolysis is not continued too far. The change in concentration in the anode and the cathode compartment naturally depends on the velocity of the ions leaving their chambers. Thus

$$\frac{\textit{equivalent mass of electrolyte lost at anode compartment}}{\textit{equivalent mass lost at cathode compartment}} = \frac{u_+}{u_-} \tag{14.22}$$

and the total loss, therefore, shall be proportional to $u_+ + u_-$. Consequently t_- and t_+ will be given by

$$t_- = \frac{\textit{equivalent mass lost in cathode chamber}}{\textit{total loss in anode and cathode chamber in equivalent mass}} \tag{14.20}$$

since $$t_- = \frac{u_-}{u_+ + u_-}$$

and similarly

$$t_+ = \frac{\textit{equivalent mass lost in anode chamber}}{\textit{total loss in the anode and cathode in equivalent mass}} \tag{14.21}$$

It is needless to say that if u_+ and u_- are equal then $t_+ = t_- = 0.50$. The above relations show that if the change of concentration around anode or cathode resulting from electrolysis can be measured the transport number of the ions can be found out.

In many instances the electrode itself takes part in the electrolysis. For example, if silver nitrate is electrolysed between silver electrodes the electrodes will go into solution. This will result in an increase, rather than a decrease, in concentration at the anode chamber. The amount of silver dissolved will be governed by Faraday's laws of electrolysis and may be determined by placing a coulometer in the circuit. The loss of electrolyte due to migration can then be calculated from the initial concentration, final concentration and the amount of material deposited or dissolved.

14.18 Measurement of Transport Number

Transport number may be measured by different methods, e.g. Hittorf's method, moving boundary method and from the electromotive force of concentration cells.

(a) Hittorf's method: This method is based on the measurement of change in the concentration of the electrolyte in the neighbourhood of the cathode and the anode as a result of the passage of electricity. The form of the apparatus usually used in the laboratory for the purpose is shown in Figure 14.14. It consists of three parts which can be separated from one another by means of the stop-cocks *SS*. The parts can be named the cathode chamber, the anode chamber and the middle chamber. The chambers are provided near the bottom with stop-cock S_1, S_2, S_3, through which liquids can be drained off. Electrodes are inserted into the cathode and anode chambers. The electrodes are connected to a *d-c* supply source *B*, through a variable resistance *R*, a milliammeter *mA* and a copper or silver coulometer (not shown in the Figure). The latter is for measuring the quantity of electricity passed. The method of measurement may be illustrated by the determination of transport number of silver and nitrate ions. In this case the electrodes consist of stout silver wires.

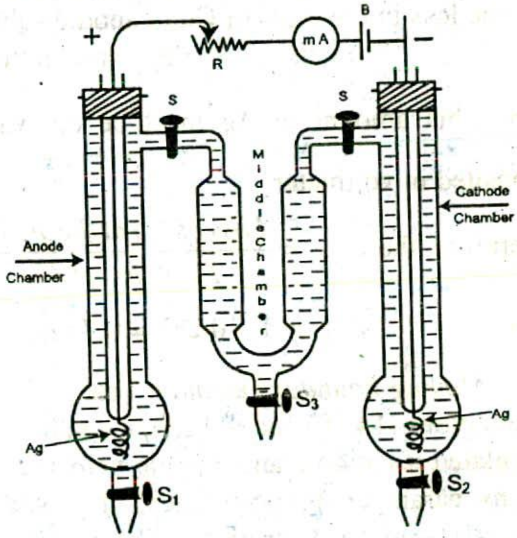


Figure 14.14 Hittorf's apparatus

The transport number tube is filled with a dilute $AgNO_3$ solution of exactly known concentration (0.1– 0.05 $mol\ L^{-1}$). All air bubbles are carefully removed. A small current (10-20 *mA*) is passed through the solution for a known period, say two hours. Any fluctuation in the milliammeter reading is adjusted by the variable rasistance *R* to maintain steady value of the current. From the time and the current the total quantity of electricity in Coulomb passed through the solution is calculated. This is checked with the coulometer in the circuit. As a result of passing the current electrolysis takes place, *Ag* is deposited on the cathode and dissolved in the anode.

However, due to migration of ions, the concentration of the solution in the anode chamber and in the cathode chamber has changed but that in the middle chamber remains unchanged (*Section 14.17* and Figure 14.14). Immediately after stopping the current the stop-cocks *SS* are closed to prevent diffusion. The solutions from the anode and the cathode chambers are separately taken out by opening stopcocks, S_1 and S_2. These solutions are separately weighed in two different bottles and analysed for silver content, usually by titrating against standard NH_4SCN solution with ferric alum as indicator. Since the initial concentration of the $AgNO_3$ is known the fall in concentration in cathode and anode chambers are calculated.

Example 14.10: A dilute solution of $CuSO_4$ was electrolysed using two Pt electrodes. The amount of Cu per unit mass of the anodic solution was found to be 0.6350 and 0.6236 g after and before electrolysis respectively. The amount of Ag deposited in silver coulometer in the series was 0.1351 g. Calculate the transport numbers of Cu^{2+} and SO_4^{2-} ions. (RAM of $Cu = 63.5$ and $Ag = 107.88$)

Solution:

The mass of Cu^{2+} in anodic solution before electrolysis = 0.6350 g

And, the mass of Cu^{2+} in anodic solution after electrolysis = 0.6236 g

So, the loss in the mass of Cu in anodic solution = (0.6350 – 0.6236) = 0.0114 g

The mass of Ag deposited in the voltmeter = 0.1351 g

Now, this amount of Ag must be equivalent to $\dfrac{0.1351\times(63.5/2)}{107.88} = 0.0397$ g of Cu deposited in voltmeter.

Therefore, the $t_{Cu^{2+}} = \dfrac{\textit{Loss of Cu at the anode}}{\textit{Total loss of Cu}} = \dfrac{0.0114}{0.0397} = 0.287$

And $t_{SO_4^{2-}} = 1 - 0.287 = 0.713$

(b) Moving boundary method: From the very definition of transport numbers as shown in equations (14.20) and (14.21), it can be seen that transport number may be directly calculated if cationic and anionic velocities or any parameter proportional to the ionic velocities can be determined. The moving boundary method utilizes this principle. The arrangement is shown in Figure 14.15. The solution of an electrolyte MA, which is to be studied, is placed between the solutions of two other salts MA' and $M'A$ such that $M'A$ has the anion A common with MA and MA' and MA have the common cation M. The salts are to be so chosen that the densities increase downwards. Also, the speed of the ion M' should be less than that of M while the speed of A' should be less than that of A ion.

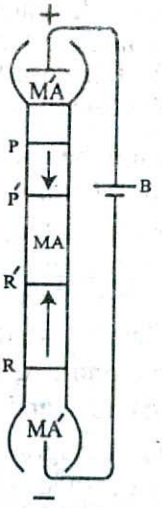


Figure 14.15 Moving boundary method

This is essential to maintain sharp boundaries between the three solutions of electrolytes. The initial sharp boundary between the solutions of $M'A$ and MA is shown by the horizontal line P whereas the initial sharp boundary between MA' and MA is shown by R. In passing current from the source B ionic migration starts and the boundary P moves downwards, say to P', while the boundary R moves to R'. The distance travelled by the two boundaries in time t are PP' and RR', which are directly proportional to the cationic and anionic velocities respectively. Therefore,

$$t_+ = \frac{u_+}{u_- + u_+} = \frac{PP'}{PP'+RR'} \tag{14.23}$$

$$t_- = \frac{u_-}{u_+ + u_-} = \frac{RR'}{PP'+RR'} \tag{14.24}$$

The transport numbers are thus measured. It should be noted that electrolytes MA, MA' and $M'A$ should be carefully chosen to get good results. In practice it is necessary to form one boundary and observe the rate of its movement to measure the transference number of one ion; that of the other ion may then be calculated as $t_+ + t_- = 1$.

Under this condition the transference number is calculated as follows: Suppose that the boundary of the moving cation is swept through a distance l in a tube of cross section a, so that the volume swept out by the passage of Q coulombs of electricity is $l \times a$. If $1F$ of electricity flows through the solution t_+ *equivalent mass* of cation must pass through any given point. Let c, be the concentration of the solution in *equivalent mass* L^{-1}; then the volume of solution containing 1 *equivalent mass* of electrolyte is 1000/c. Hence during the passage of 1 F of electricity the cation boundary will sweep through a volume $\frac{1000}{c}$ t_+. For the passage of Q coulombs, therefore, the same boundary will sweep out a volume of

$$\frac{1000 \times t_+ \times Q}{c \times F}$$

Hence $$l \times a = \frac{1000 \times t_+ \times Q}{c \times F}$$

or, $$t_+ = \frac{l \times a \times c \times F}{1000\,Q}$$

Examle 14.11: A moving boundary experiment was carried out with 0.100 $mol\ L^{-1}$ HCl solution with $CdCl_2$ as the indicator electrolyte. The boundary moved through a distance of 6.50 cm in a tube of cross section 0.11 cm^2. If a constant current of 0.0056 A was passed for 2100 seconds, calculate the transport numbers of H^+ and Cl^- ions.

Solution: Here $a = 0.11$ cm^2, $l = 6.50$ cm, $c = 0.100\ mol\ L^{-1}$

Or, $$t_{H^+} = \frac{l \times a \times c \times F}{1000\,Q} = \frac{0.11 \times 6.5 \times 0.1 \times 96500}{1000 \times 0.0056 \times 2100} = 0.5867$$

$$t_{Cl^-} = 1 - 0.5867 = 0.4133$$

14.19 Factors Affecting Transport Numbers

The transport number of ions varies with change of concentration; such changes are quite complicated and the extent of change is also small. Transport number also depends on the temperature; t_+ usually increases slightly with rise of temperature. The anion transport number, therefore, generally decreases with increase of temperature. In Table 14.8 the transport numbers of some cations are given.

Table 14.8 Cation Transport Number at 20°C

Electrolyte	t_+	Electrolyte	t_+
HCl	0.823	$ZnSO_4$	0.395
$LiCl$	0.338	$CuSO_4$	0.397
$NaCl$	0.395	$BaCl_2$	0.449
KCl	0.490	$AgNO_3$	0.461
KBr	0.488	K_2SO_4	0.483
KNO_3	0.508	$MgSO_4$	0.395
$CsCl$	0.501	$Ba(NO_3)_2$	0.465
KI	0.487	$MgCl_2$	0.402

For the same cation or the anion the transport number depends on the electrolyte. Thus t_+ values for K^+ in KCl, KBr and KNO_3 are 0.490, 0.488 and 0.508 respectively. Similarly t_- values for Cl^- in HCl, $LiCl$, $NaCl$ and KCl are 0.177, 0.662, 0.605 and 0.510 respectively. This is easy to understand because the transport number is not a unique property of the ion but depends on the relative speeds of the cation and anion in an electrolyte.

Abnormal Transport Numbers: It is sometimes found that the transport numbers of some ions decrease rapidly with increase in concentration of the ions. Examples are the transport number of silver in ammoniacal solution, cadmium in cadmium iodide. This change in transport number is attributed to complex formation, whereby the metallic ion forms a part of a complex anion and travels to the anode. For cadmium this is represented as follows:

$$2CdI_2 \rightleftharpoons Cd^{2+} + [CdI_4]^{2-}$$

QUESTIONS AND PROBLEMS

1. What are electrolytes? Distinguish between strong and weak electrolytes.
2. State four ways in which metallic and electrolytic conduction differ.
3. Write a short essay on the theories of electrolytic dissociation. What is the modern concept about strong electrolytes?
4. State Faraday's Laws of electrolysis and explain these clearly. Describe experiments by which the laws can be verified.
5. Explain the terms (i) Faraday, (ii) Coulomb, (iii)) Coulometer.
6. How does a coulometer work? What advantages are there to the use of a coulometer?
7. How many grams of O_2 and H_2 are produced in 1.0 hour when water is electrolysed at a current of 0.50 A? What would be the volumes of the two gases measured at STP?
8. 200 *mL* of 0.1 *mol* L^{-1} solution of $AgNO_3$ is electrolysed by a current of 0.2 ampere. How many minutes will be required to deposit half the silver in the solution on the cathode? [Ans. 80 min 25 sec]
9. Explain clearly conductivity and specific conductance.

10. Describe a suitable experiment by which the specific conductance of an electrolyte solution can be measured. Why is it necessary to use an *a-c* current source?

11. What is cell constant? State its unit.
A solution of 0.01 $mol\ L^{-1}$ KCl had a resistance of 1748.6 ohm at 25°C in a certain conductance cell. Given that the specific conductance of the above KCl solution is $1.411 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$, calculate the cell constant of the working cell. [Ans. 2.47 cm^{-1}]

12. A conductance cell was calibrated by filling it with 0.02 $mol\ L^{-1}$ solution of KCl ($\kappa = 2.768 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$) and measuring the resistance at 25°C, which was found to be 457.3 ohm. The cell was then filled with a calcium chloride solution containing 0.555 g $CaCl_2$ per litre. The measured resistance was 1050 ohm. Calculate (a) the cell constant of the cell, and (b) specific conductance of the $CaCl_2$ solution. [Ans. (a) 1.266 cm^{-1}, (b) $1.206 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$]

13. The resistance of a conductivity cell containing 0.020 $mol\ L^{-1}$ KCl is 102 ohms at 18°C. The specific conductance of this KCl solution at 18°C is 0.002394 ohm^{-1}. Calculate the cell constant. [Ans. 0.2442 cm^{-1}]

14. What is meant by molar conductance? What is the significance of molar conductance at infinite dilution? How does molar conductance vary with electrolyte concentration for (a) strong electrolytes and (b) weak electrolytes?

15. Describe how Debye-Huckel theory explains the variation of molar conductance of strong electrolytes with concentration.

16. What is conductance ratio? Describe how the degree of dissociation of weak electrolytes may be determined?

17. Show how the dissociation constant of a weak acid can be calculated from conductance measurement.
Formic acid is 7.2% dissociated in a 0.1 $mol\ L^{-1}$ solution at 20°C. Calculate the dissociation constant of the acid.

18. What is ionic mobility and how can this be measured?

19. State and explain the principle of independent ionic migration and mobility. Explain the relation

$$\lambda_+^0 + \lambda_-^0 = \Lambda^0 .$$

20. Calculate the conductance at 25°C of solution containing 0.001 $mol\ L^{-1}$ HCl and 0.005 $mol\ L^{-1}$ $NaCl$. The values of ionic conductance at infinite dilution may be used. [Ans. $1.058 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$]

21. Explain the conductance behaviour of a system where (a) a strong acid is titrated with a strong base and (b) a weak acid is titrated with a strong base. Explain your answer with suitable graphical representations.

22. What are the advantages of conductometric titrations over ordinary titrations? Explain your answer with suitable examples.

23. Explain clearly the term 'Transport Number'. Describe one method for measurement of transport number.

24. Will the transport number of chloride ion be the same in HCl, $LiCl$, KCl and $CuCl_2$? If not, explain how the transport number will change and why?

25. Describe Hittorff's method for measurement of transport number of Ag^+ in $AgNO_3$ solution.

26. A moving boundary experiment was carried out with a 0.10 $mol\ L^{-1}$ solution of HCl at 25°C. Sodium ions are caused to follow hydrogen ions under a potential gradient of 1.76 $V\ cm^{-1}$. Three milliamperes current are passed through the tube of 0.3 cm^2 cross-sectional area, and it is observed that the boundary moves 3.08 cm in 1.0 hour. Calculate the hydrogen ion mobility. Given that the chloride ion mobility is $7.64 \times 10^{-4}\ cm\ V^{-1}\ s^{-1}$ calculate the transport number of hydrogen ions. [Ans. $36.3 \times 10^{-4}\ cm\ V^{-1}\ s^{-1}$; $t_{H+} = 0.83$]

27. A saturated solution of $AgCl$ in water had a specific conductance of $3.4 \times 10^{-8}\ ohm^{-1}\ cm^{-1}$ and the specific conductance of water at the same temperature was $1.6 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$. Calculate the solubility of $AgCl$. Given $\lambda°_{Ag+} = 61.9\ ohm^{-1}\ cm^2$ and $\lambda°_{Cl^-} = 76.3\ ohm^{-1}\ cm^2$. [Ans. $1.88 \times 10\ g\ L^{-1}$]

28. Molar conductances at infinite dilution of $Ca(OH)_2$, $CaCl_2$ and NH_4Cl are 258, 136 and 150 respectively, all in units of $cm^2\ mol^{-1}\ ohm^{-1}$. Calculate the molar conductance at infinite dilution of NH_4OH at 25°C. [Ans. $\Lambda° = 272\ cm^2\ mol^{-1}\ ohm^{-1}$]

29. A moving boundary experiment was carried out with 0.01 $mol\ L^{-1}$ solution of KCl with $CdCl_2$ as indicator electrolyte. A current of 5.21 mA was passed through a tube of cross sectional area 0.230 cm^2 for 60 seconds when the boundary moved a distance of 4.16 cm. Calculate the transport numbers of the ions. [Ans. $t_{K^+} = 0.1772$, $t_{Cl^-} = 0.8227$]

30. In an electrolysis experiment with a 0.1 $mol\ L^{-1}$ solution of $AgNO_3$ using two Pt electrodes it was found that a fall of concentration of $0.5124 \times 10^{-3}\ g$ occurred in the anodic solution in 120 seconds after passing a small current. The mass of Cu deposited in a copper coulometer placed in series was found to be 0.03879 g. Calculate the transport numbers of Ag^+ and NO_3^- ions. [Ans. $t_{Ag^+} = 0.42$, $t_{NO_3} = 0.58$]

15 ELECTROCHEMICAL CELL

We are all too familiar with electricity. Life in these days of technological marvel would have been quite different without the help of electrical energy. The area of chemistry that deals with the inter-conversion of electrical energy and chemical energy is known as *electrochemistry*. Electrochemical processes involve *redox* reactions in which energy released by spontaneous chemical reactions is converted into electricity. The present chapter includes the fundamental principles and applications of galvanic cells and the thermodynamics of electrochemical cells.

15.1 Galvanic Cells

An electrochemical cell is an arrangement in which electric energy is released by a spontaneous *redox* reaction. This kind of cell is also known as Galvanic cell or Voltaic cell named after two Italian scientists Luigi Galvani (1780) and Alessandro Volta (1800) who first conducted several experiments on chemical reactions and electric current. A common example of such a cell is *Daniel Cell*. A schematic diagram of the Daniel cell is given in Figure 15.1.

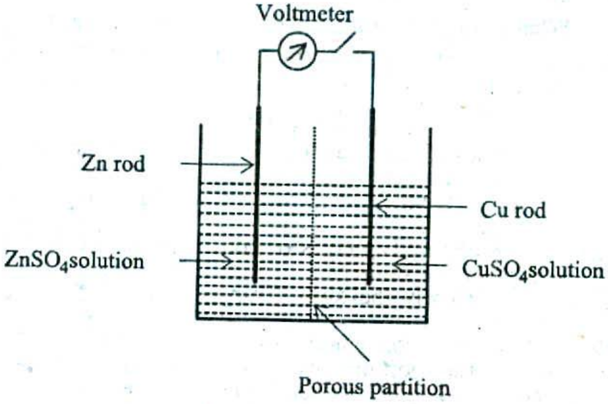


Figure15.1 Schematic diagram of Daniel cell

The cell essentially consists of a zinc rod dipped into a solution of zinc sulphate and copper rod dipped into a solution of copper sulphate, the two solutions being separated by a porous partition which allows the solutions to come in contact with each other but prevents complete mixing from taking place. As already mentioned (Chapter 14) the electrodes are metal wires/rods/sheets/bars which are dipped into the solutions. When the two electrodes (zinc and copper rods) are connected externally by a wire, electric current flows (as shown by the ammeter). Zinc dissolves from the zinc rod giving zinc ions whereas copper ions deposit on the copper rod as metallic copper. A voltmeter (not shown in the Figure) placed in the circuit measures the potential difference between the two electrodes. This is the *electro motive force (e.m.f.)* of the cell.

The reactions taking place in a Daniel cell can be split up into two parts taking place at the two electrodes, each reaction being known as a *half-reaction*. At the zinc electrode oxidation takes place. So it is the anode: electrons released at this electrode move through the wire as indicated in Figure 15.1 to the copper electrode (which is the cathode) where these combine with copper ions to produce copper by reduction. As long as the electrodes are connected by a wire, electrons will be released at the anode and flow to the cathode (current will pass) until either zinc rod or copper ions are exhausted. Equations for the two half – reactions are shown below:

$$\textit{Zinc electrode (anode)} \quad : Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \tag{15.1}$$

$$\textit{Copper electrode (cathode)}: Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \tag{15.2}$$

The sum of reactions (15.1) and (15.2) gives the complete cell reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \tag{15.3}$$

15.2 The Origin of E.M.F. at Metal-Solution Interface

Mention has been made of the potential difference between the electrodes. The question one may ask is: what is meant by the term potential of the electrode and how does the potential difference arise?

The origin of the potential difference between the two electrodes may be traced to the relative tendencies of zinc and copper, or any other metal to go into solution as ions. Zinc has a greater tendency to form ions than copper; that is why this familiar fact that when a zinc rod is dipped into a copper sulphate solution a deposit of copper metal is obtained. Nernst supposed that whenever an electrode is immersed into an electrolytic solution containing its ions (say copper electrode dipped into a solution containing Cu^{2+} ions), there is a tendency of the electrode metal to go into solution as ions. This is opposed by the positive charge on the ions. As the concentration of the metal ions in solution increases this opposition increases, and the reverse process of deposition of positive ions on the electrode starts taking place. An equilibrium is finally reached when the rate at which the ions are formed is equal to the rate at which the ions are deposited. The equilibrium can be represented as:

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

A potential develops at the *interface* between the solid electrode and the electrolyte solution. This potential is called *electrode potential*. The *electrode potential* indicates the tendency of an electrode either to lose or gain electrons in the electrode reactions. More precisely, it is the potential difference of the electrical double layer formed at the contact interface of electrode metal and the electrolytic solution. It is also called *single electrode potential*.

From the above kinetic viewpoint Nernst derived the relation

$$E = E^{\circ} + \frac{RT}{nF} \ln [M^{n+}] \tag{15.4}$$

for the electrode potential, E. Here $[M^{n+}]$ is the concentration of the ion of valence n, T is the temperature in K, R is the universal gas constant and F is the Faraday. $E°$, which is called the *standard electrode potential*, is the value of E when $[M^{n+}]$ is unity. So one can say that

The standard potential of an electrode is the potential difference between a metal and its ions in solution of concentration one mol L^{-1}.

Standard electrode potentials are used to compare the tendency of the metal to lose electrons or gain electrons.

As we shall see in *Section 15.13* the equation shown above is the same as the one derived thermodynamically except that the concentration is replaced by activity. Equation (15.4) is known as the Nernst equation.

15.3 Reversible and Irreversible Cells

A Galvanic cell always has two electrodes in which there is difference in the tendency to give up electrons. The electrodes are properly arranged so that current can flow. Galvanic cells may be either reversible or irreversible in the thermodynamic sense. A *reversible cell* is one which does not give any current when it is connected in an opposite sense to an outside source of *e.m.f.* exactly equal to that of the cell. If the *e.m.f.* of the external source is infinitesimally higher than that of the cell then the current will go in the opposite direction, i.e., the cell reaction will be reversed ; on the other hand, if the value is slightly lower current will flow from the cell. Daniel cell is an example of a reversible cell.

When in a cell reaction a gas is evolved or a precipitate is formed the cell is irreversible because the cell cannot be brought back to its original condition by reversing the current. As an example of an irreversible cell consider zinc and copper electrodes which dip into a solution of sulphuric acid. When the cell is producing current the cell reaction will be

$$Zn\,(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2\,(g) \qquad (15.5)$$

The zinc electrode dissolves to form zinc ions, and hydrogen is liberated at the copper electrode. When the current is reversed the above reaction is not reversed. Instead the following reaction takes place

$$Cu\,(s) + 2H^+(aq) \rightleftharpoons Cu^{2+}(aq) + H_2(g) \qquad (15.6)$$

Copper goes into solution and hydrogen gas is liberated.

Irreversible cells are not amenable to exact theoretical treatment. For reversible cells thermodynamic principles may be applied as will be shown in *Section 15.15*. The work done in a reversible cell is the maximum and the maximum work can be related to other thermodynamic quantities. In reversible cells both the electrodes are reversible with respect to one or other of the ions in solution.

15.4 Measurement of E.M.F of Electrochemical Cells

When current is drawn from a cell its *e.m.f.* gradually drops as chemical energy is being converted into electrical energy. In order to obtain correct *e.m.f* of the cell the measurements should be carried out in such a way that no current is drawn from the cell. Since this is not possible in practice, the measurement is carried out under conditions in which the current drawn from the cell is so small as to be negligible. The principle of the method was first described by Poggendorf and the method is known as the *Poggendorf's compensation method.* In this method the unknown *e.m.f.* of a cell is opposed by a cell of known *e.m.f.*, and hence the name *compensation method.* The electrical circuit he used is known as a *potentiometer circuit.*

The basic potentiometer circuit is shown in Figure 15.2. AB is a wire of uniform resistance. The ends A and B of the wire are connected to the two electrodes of a lead storage battery, C, through a variable resistance, R. Along the wire AB there is a gradual fall of potential which is proportional to the length of the wire. One electrode of the cell, E, whose *e.m.f.* is to be measured, is connected through a galvanometer, G, to A. The other electrode is connected through a key, K, to AB by a sliding contact D.

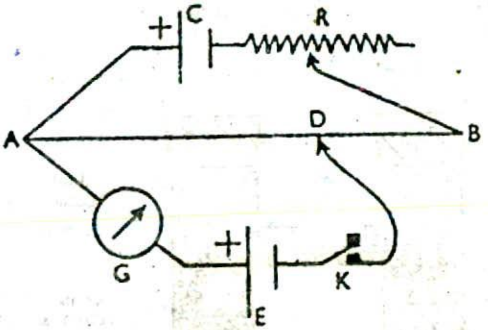


Figure 15.2 Principle of a potentiometer

After pressing the key K the contact D is moved along the wire until there is no deflection of the galvanometer, indicating that no current is flowing. At this position the fall of potential along the wire AB from A to D is equal to the potential of the cell E. If now the cell E is replaced by a standard cell, S, the potential of which is very accurately known, a new position of the contact, D′, is found when no current flows through the galvanometer. At this position

$$\frac{\textit{Length of the wire with cell E}}{\textit{Length of the wire with standard cell S}} = \frac{\textit{Potential of the cell E}}{\textit{Potential of the standard cell S}} \tag{15.7}$$

From the known value of the potential of the standard cell, S, and the experimentally determined value of the lengths of wire, the potential of the cell, E, may be obtained.

Alternately a *high resistance voltmeter* could be connected to the two electrodes of the two half – cells and the *e.m.f.* of the cell is read directly. A high resistance voltmeter allows only small amount of current to pass and does not change the concentrations of the electrolytes significantly.

For actual measurements an instrument called the potentiometer is used. The basic principle is the same as above but instead of the length of wire there are two circular resistances, R_1 and R_2, as shown in Figure 15.3, *which are directly calibrated in volts.*

The instrument is first set by placing a standard cell in the circuit, setting the dials for R_1 and R_2 to read the potential of the standard cell, and adjusting the variable resistance, R, so that no current passes through the galvanometer, G. The standard cell is now replaced by the experimental cell and keeping the setting of R fixed the dials for R_1 and R_2 are adjusted until again no current passes through the galvanometer. The *e.m.f.* of the cell is read off directly from the dials for R_1 and R_2. This method is capable of giving results of high accuracy.

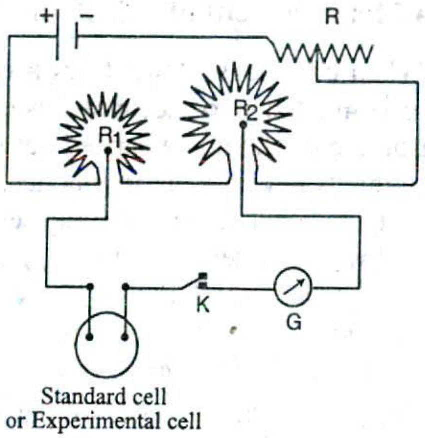


Figure 15.3 E.M.F. measurement with a potentiometer

15.5 Weston Standard Cell

The accuracy of measurement of *e.m.f.* of a cell by the Poggendorf method depends on the constancy of the potential of the standard cell, provided the galvanometer used is a sensitive one. A standard cell will maintain a constant and reproducible *e.m.f.* provided that very little current is drawn from it. Another condition is that the *e.m.f.* should be affected by temperature only slightly. The standard cell usually employed in potentiometric measurements is the Weston cadmium cell, shown in Figure 15.4.

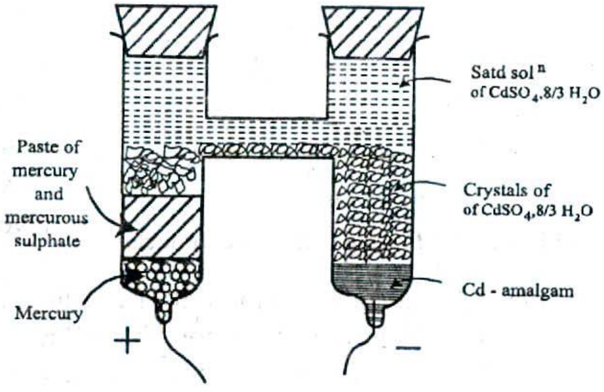


Figure 15.4 Standard Weston cell

One limb of the H-shaped vessel contains mercury over which is placed a paste of mercurous sulphate and mercury. In the other limb is placed a cadmium amalgam. The rest of the vessel is filled with a saturated solution of cadmium sulphate containing an excess of solid $CdSO_4$, $8/3\ H_2O$ crystals. The reaction taking place in the cell when it is producing current is

$$Cd(s) + Hg_2SO_4(s) + aq \rightleftharpoons CdSO_4, 8/3\ H_2O(s) + 2Hg(l) \tag{15.8}$$

The potential of the cell is 1.0183 V at 25°C and it has a very small temperature coefficient.

15.6 Types of Half-Cells

The reaction taking place in an electrochemical cell may be split up into two reactions at the two electrodes. Similarly, the cell may be split up into two half-cells, one at each electrode; an electrode dipping into a solution is said to constitute a half-cell. Thus in the Daniel cell $Zn \mid Zn^{2+}$ and $Cu \mid Cu^{2+}$ constitute two half-cells. It is convenient to describe the electrochemical processes in terms of half-cells, as two half-cells can be suitably arranged to produce a desired reaction in a cell. Various types of reaction may be made to occur electrochemically and various electrodes or half-cells may be used. Some of these are described here.

Metal-metal ion electrode: This is the simplest type of electrode where a metal is dipped into a solution of its ions. Examples are silver in silver nitrate solution, copper in copper sulphate solution. The silver-silver ion electrode is represented as $Ag \mid Ag^+$ and the copper-copper ion electrode as $Cu \mid Cu^{2+}$.

The electrode reactions are $Ag^+ + e^- \rightleftharpoons Ag$ and $Cu^{2+} + 2e^- \rightleftharpoons Cu$ respectively. The electrodes are reversible with respect to the metal ions.

Amalgam electrode: In many cases it is convenient to form the metal electrode by using an amalgam, i.e., a solution of the metal in mercury. An example is the Cd-amalgam electrode used in the Weston standard cell (*Section 15.5*). As shown in Figure 15.4 electrical contact is made by a platinum wire immersed in the amalgam. The reaction is the same as in the metal-metal ion electrode. An amalgam electrode is of importance in those cases where the metal is too reactive to be used in the pure form. For example, one cannot make a sodium electrode with the pure metal as sodium reacts with water, but a sodium amalgam electrode may be set up easily. Unless the amalgam is saturated with respect to the solute metal the concentration of solute metal in the amalgam as well as the concentration of the metal ion must be given as the *e.m.f.* of the electrode depends on both. A sodium amalgam half-cell is represented as

$$Na - Hg(c_1) \,\big|\, Na^+(c_2)$$

Metal-insoluble salt electrode: This consists of a metal in contact with an insoluble salt of the metal which, in turn, is in contact with a solution containing the anion of the insoluble salt. An example is the silver, silver chloride electrode represented as

$$Ag, AgCl\,(s) \mid Cl^-(c_1)$$

The electrode reaction can be considered as taking place in two steps:

$$\begin{array}{c} Ag(s) \rightleftharpoons Ag^+(aq) + e^- \\ Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \\ \hline Ag(s) + Cl^-(aq) \rightleftharpoons AgCl(s) + e^- \end{array} \qquad (15.9)$$

The electrode reaction involves only the concentration of Cl^-; the electrode is said to be reversible with respect to Cl^-. The above reaction shows how an electron can be released or taken up in such an electrode. Another example of metal insoluble salt electrode is the mercury, mercurous sulphate electrode $Hg,\ Hg_2SO_4\ (s) \mid SO_4^{2-}\ (c)$ used in the standard Weston cell.

The most frequently used electrode of this type is the calomel electrode, which consists of mercury in contact with mercurous chloride (calomel) as a paste, over which is placed a solution containing chloride ions, usually KCl. The electrode which is represented as $Hg,\ Hg_2Cl_2(s)/Cl^-(c)$ is shown in Figure 15.5. The electrode is usually made with 0.1 $mol\ L^{-1}$ or saturated KCl solution. A paste of mercury and calomel is first made by thorough grinding. This is then washed several times with small portions of the KCl solution. The paste is placed in the clean electrode vessel in which some amount of pure mercury had already been placed. The rest of the vessel is then filled with the KCl solution. A tube at the end of which a piece of platinum wire is sealed is placed in the vessel as shown in Figure 15.5.

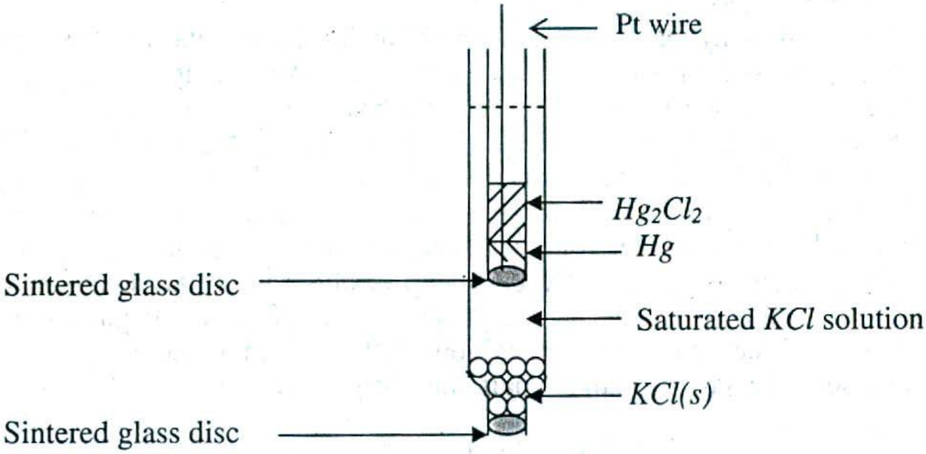


Figure 15.5 Saturated calomel electrode

Some mercury is placed in this tube. Contact with mercury in the vessel is made by dipping a thick copper wire in the mercury in the tube.

Oxidation-reduction electrode: This name is generally used for electrodes in which an inert metal dips into a solution containing ions of the same element in two different oxidation states. An example is the half-cell $Pt|Fe^{2+},\ Fe^{3+}$ in which the following reaction takes place

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$

It will be recalled that in all electrodes either oxidation or reduction takes place. The difference between an oxidation-reduction electrode and other electrodes, e.g., a $Ag|Ag^+$ electrode, is that whereas in the latter the *e.m.f.* depends only on the concentration of the silver ions, in the former the *e.m.f.* is dependent on the concentration of the ion in both the oxidation states.

Gas electrodes: These electrodes are prepared by dipping a foil of an inert metal like platinum or gold in a solution and bubbling the gas over the surface of the foil. An example is the hydrogen electrode represented as

$$Pt, H_2 (P\ atm) \mid H^+(c)$$

It consists of a *platinized* (platinum foil on which platinum has been deposited electrolytically) platinum foil dipped into a solution containing hydrogen ions and a stream of hydrogen gas at a pressure P atm is bubbled through the solution on the surface of platinum. The arrangement is shown in Figure 15.6. Usually the vessel is open to the atmosphere so that the gas is at atmospheric pressure. The reaction at the hydrogen gas electrode may be written as

$$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$$

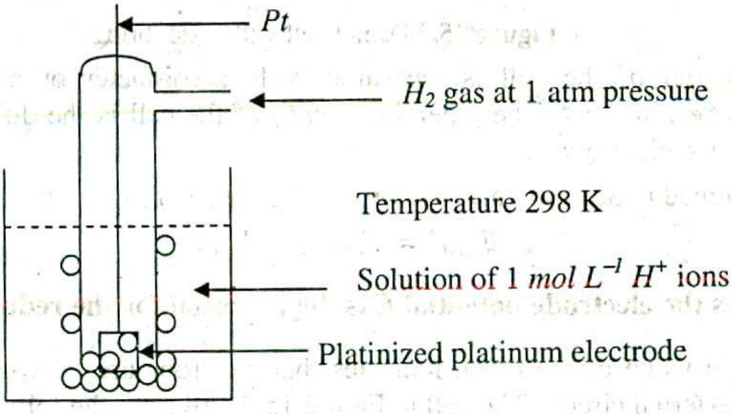


Figure 15.6 Standard hydrogen electrode

15.7 Single Electrode Potential: Standard Hydrogen Electrode

The potential of a single electrode (half-cell) can not be measured directly because for measuring potential there has to be flow of current. For current to flow there has to be two electrodes with difference of potential between the two and these have to be correctly connected. This is similar to a situation where there will be no flow of water between two reservoirs unless there is difference in water level between the reservoirs.

To measure the potential of an electrode a cell has to be set up with two electrodes as shown in Figure15.7. The connection between the solutions in the two electrode compartments are made with a **salt bridge.** *A salt bridge is a doubly bent tube (as shown) containing a solution of KCl, or KNO_3 or NH_4NO_3 and closed at the two ends by cotton wool so that when inverted the solution does not fall down.* The salt bridge is placed so that the liquids in the two half–cells are connected as shown for Daniel cell in Figure 15.7. *The salt bridge allows the flow of ions but prevents the mixing of the different solutions. Such mixing would allow direct reaction of the cell reactants.* Salt bridge is also made by placing one of the above electrolyte in a gel in the tube. *The above mentioned electrolytes are used because in each case the speed of movement of the cation and the anion are almost same.*

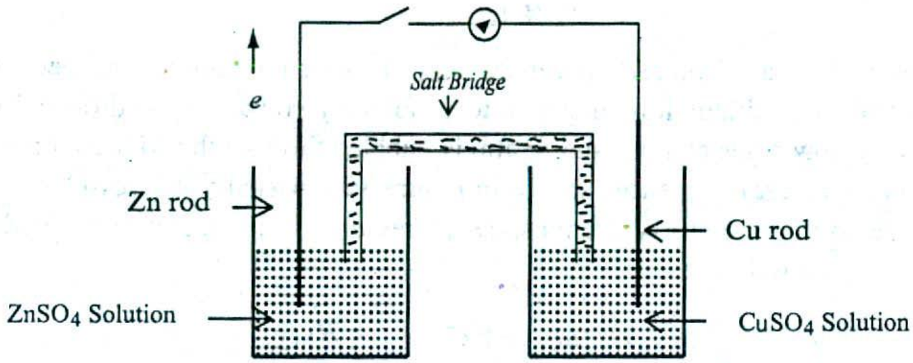


Figure 15.7 Daniel cell with a salt bridge

The potential of the cell is measured with a voltmeter or a suitable device as described in *Section 15.4*. The potential (*e.m.f.*) of the cell is the difference of potential between the two electrodes.

As mentioned in *Section 15.9*, by convention the *e.m.f.*, *E*, of the cell is written as

$$E_{cell} = E_{cathode} - E_{anode}$$

In both cases the electrode potential *E* is the potential for the reduction reaction.

A positive value of the *e.m.f.* indicates that electrons are flowing from left to right through the external circuit. The cell in Figure 15.7 will have the following *e.m.f.*

$$E_{cell} = E_{Cu^{2+},Cu} - E_{Zn^{2+},Zn}$$

If the potential of one of the electrodes is known the other can be found out. For this purpose a *reference electrode* is used whose potential is known.

The standard hydrogen electrode (SHE) is used as a reference electrode. The reduction potential of the standard hydrogen electrode has been arbitrarily taken as 0.00 V by convention.

The standard hydrogen electrode (shown in Figure 15.6) is set up as follows:

A platnized platinum foil is immersed in an acid solution in which the concentration of H^+ ion is 1.0 $mol\ L^{-1}$ and dry hydrogen gas at a pressure of 1.0 atm is bubbled over the foil at a temperature of 25°C. The following equilibrium is established on the surface of the platinum:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

15.8 Secondary Standard Electrodes

The hydrogen electrode is not a convenient reference electrode to use in measurement for the following reasons:

(i) One has to prepare a *SHE* every time it is needed; the procedure is cumbersome.
(ii) Maintaining a stream of hydrogen at 1 atm takes careful arrangement,
(iii) Preparation of a solution of an acid in which the concentration of H^+ ion is exactly 1.0 $mol\ L^{-1}$ is time consuming.
(iv) It is not easy to prepare pure hydrogen.
(v) Hydrogen has to be handled very carefully as it is inflammable.

In order to avoid these difficulties other electrodes that can be prepared easily and whose electrode potentials are constant under certain conditions have been devised. Such electrodes are known as *secondary standard electrodes*. Two such electrodes are:

(a) Calomel electrode and
(b) Silver electrode.

15.8.1 Calomel electrode

Calomel electrode has been discussed in *Section 15.6* and a schematic diagram is shown in Figure 15.5. The electrode is represented as

$$Pt\,/Hg, Hg_2Cl_2(s)\ \ KCl\,(satd.)\,(aq)$$

The electrode reaction is

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

The potential of saturated calomel electrode is 0.244 V.

15.8.2 Silver – silver chloride electrode

This electrode is prepared by dipping a silver rod into a saturated solution of potassium chloride over a paste of AgCl and is represented as

$$Ag\,/AgCl(s),\ Cl^-\ (satd)\ (aq)$$

The electrode reaction is

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

15.9 Electrochemical Cells: Notations and Sign Convention

An electrochemical cell may be prepared by combining any two half–cells. Such cells and half-cells are conveniently described by an abbreviated notation together with appropriate conventions so that the convention will correspond to the chemical reaction taking place in the cell. Moreover, the conventions used for the cells must be compatible with other thermodynamic conventions. The following notations are used by convention for describing cells and half–cells:

1. The half-cells written in the sequence *electrode* | *electrolyte* represents oxidation and if the sequence is *electrolyte* | *electrode*, it means reduction. Examples are:

$Ag(s) \mid Ag^+(aq)$	$Ag(s) \rightleftharpoons Ag^+(aq) + e^-$	Oxidation
$Ag^+(aq) \mid Ag(s)$	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	Reduction
$Ag(s) \mid AgCl(s), Cl^-(aq)$	$Ag(s) + Cl^-(aq) \rightleftharpoons AgCl(aq) + e^-$	Oxidation
$Cl^-(aq), AgCl(s) \mid Ag(s)$	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	Reduction
$Zn^{2+}(aq) \mid Zn(s)$	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	Reduction
$Pt \mid Fe^{2+}(aq), Fe^{3+}(aq)$	$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$	Oxidation
$Pt \mid Fe^{3+}(aq), Fe^{2+}(aq)$	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	Reduction
$Pt \mid H^+(aq), H_2(g)$	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	Reduction
$Pt \mid H_2(g), H^+(aq)$	$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$	Oxidation

Note that gas electrodes or oxidation-reduction electrodes have an inert metal (platinum) as the electron-carrying medium.

2. A complete cell is written such that the left hand side represents the oxidation reaction half-cell (anode) and the right hand side represents the reduction half-reaction half-cell (cathode) cell as shown below:

$$Zn(s) \mid ZnSO_4(aq) \mid CuSO_4(aq) \mid Cu(s)$$

The vertical line in the middle means that the two solutions are in direct contact. If, however, contact between the two solutions is made through a salt bridge (*Section 15.7*) two vertical lines are placed between the two electrolytes as shown below:

$$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$$

These are also written simply as

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

Examples of gas electrode and electrode with a metal in two different oxidation states are shown in a cell as below:

$$Ag(s) \mid AgCl, Cl^-(aq) \parallel H^+(aq), H_2(g) \mid Pt$$
$$Pt \mid H_2(g), H^+(aq) \parallel Fe^{2+}(aq), Fe^{3+}(aq) \mid Pt$$

3. The sign of the electrodes are opposite to those used for electrolytic cells:

Electrochemical cells	Electrolytic cells
Anode is negative	**Anode is positive**
Cathode is positive	**Cathode is negative**

4. The electrode where electron is released, i.e. oxidation takes place is written on the left side and is the anode and the cathode is written on the right side. An *e.m.f.* will be called positive if there is a tendency for electrons to be driven through the external circuit from left to right. If the cell is written such that reduction is taking place at the left hand electrode, the *e.m.f.* of the cell will be negative. The *e.m.f.* of the cell

$$Pt \mid H_2(1\ atm) \mid HCl\ (1.0\ mol\ L^{-1}) \mid AgCl(s), Ag(s) \qquad \text{(A)}$$

is = 0.2 volt, but the *e.m.f.* of the same cell written in the form

$$Ag(s), AgCl(s) \mid HCl(1.0\ mol\ L^{-1}) \mid H_2\ (1\ atm) \mid Pt \qquad \text{(B)}$$

is – 0.2 volt.

5. *For calculating the cell potential always* ***reduction potential*** *is used along with the relation*

$$E_{cell} = E_{cathode} - E_{anode} \qquad (15.10)$$

Since the anode is placed on the left hand side and cathode is placed on the right hand side the potential of the cell is also written as

$$E_{cell} = E_{cathode} - E_{anode} = E_{right} - E_{left} = E_R - E_L$$

6. If the *e.m.f.* of the cell has a positive value the cell reaction is spontaneous, i.e., if the cell works in such a way that electron is released at the left electrode and is driven through the external circuit from left to right the cell reaction will be spontaneous. In the cell (A)

At left electrode: $\frac{1}{2} H_2(g) \rightleftharpoons H^+(aq) + e^-$

At right electrode: $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$

Overall cell reaction: $\frac{1}{2} H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(aq) + Cl^-(aq)$

The potential of the cell is + 0.2 volt and so the reaction is spontaneous. It may be noted that the overall cell reaction is the algebraic sum of the reactions at the electrodes as written in the cell.

15.10 Determination of Standard Electrode Potential (SEP)

For measuring the standard potential of an electrode (which is referred to as test electrode) the test electrode is combined with a standard hydrogen electrode (SHE) to form a cell as shown in Figure 15.8.

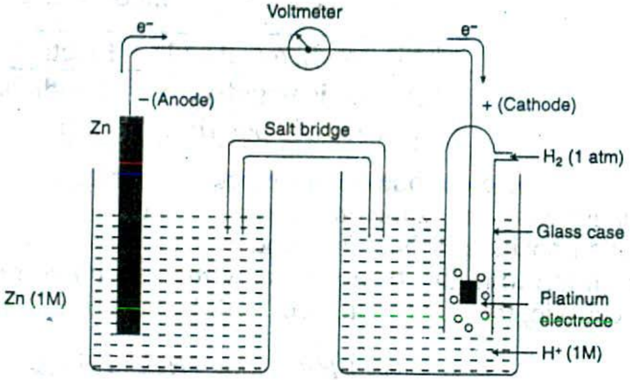


Figure 15.8 A test electrode is coupled with a standard hydrogen electrode

In the standard electrode the concentration of the ion has to be 1.0 *mol* L^{-1} and measurements have to be made at 25 °C. By convention the standard hydrogen electrode is placed on the left hand side and the test electrode on the right hand side so that the potential of the cell is given by

$$E^o_{cell} = E^o_{test\ electrode} - E^o_{SHE}$$

But $E^o_{SHE} = 0.00$. Hence $E^o_{cell} = E^o_{test\ electrode}$

In other words with this experimental set up E^o_{cell} as measured is the standard potential of the test electrode. The potential of the cell is measured with the help of a high resistance voltmeter or a digital voltmeter.

E^o_{cell} is positive if SHE is the anode, i.e., electrons flow from the left side to the right side through the external circuit and $E^o_{test\ electrode}$ is also positive. If, however, E^o_{cell} is negative then electrons flow from the right side to the left side, i.e. SHE acts as the cathode and $E^o_{test\ electrode}$ is negative. For example when the standard Zn electrode is combined with SHE the E^o_{cell} is negative. So E^o_{Zn} is negative. On the other hand, under similar conditions E^o_{Cu} is positive.

It is to be emphasized that in order to determine the cell potential the reduction potentials of both the electrodes need to be used.

Reduction potential is for reduction reaction,e.g.

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

Oxidation potential is for oxidation reaction, e.g.

$$Zn\,(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

For the same electrode system reduction and oxidation potentials are numerically equal but opposite in sign

Values of standard electrode potentials have been determined using the experimental technique described above and the data for reduction potential for some of the electrodes have been collected in Table 15.1.

15.11 Values of Standard Electrode Potentials

Various electrodes in their standard forms, i.e. using solutions of ions of concentration 1.0 *mol* L^{-1}, and gases at one atm pressure as the case may be, are combined with the standard hydrogen electrode to form cells. The potentials of the cells are measured with a high resistance voltmeter or other means. Remembering that the potential of the standard hydrogen electrode is 0.00 volt the reading in the instrument directly gives the standard potential of the electrode. All values are then converted into reduction potential and are tabulated as in a Table 15.1

Table 15.1 Standard Reduction Potentials at 25°C

Electrode	Electrode reaction	E°(V)
Li^+/Li	$Li^+ + e^- \rightleftharpoons Li$	– 3.025
K^+/K	$K^+ + e^- \rightleftharpoons K$	–2.922
Na^+/Na	$Na^+ + e^- \rightleftharpoons Na$	–2.714
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.400
$Pt, H_2O/OH^-$	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	– 0.83
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.758
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.440
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	–0.398
$Pb, PbSO_4/SO_4^{2-}$	$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$	–0.355
Tl^+/Tl	$Tl^+ + e^- \rightleftharpoons Tl$	–0.336
Co^{2+}/Co	$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.277
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	–0.250
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.140
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.126
Fe^{3+}/Fe	$Fe^{3+}\ 3e^- \rightleftharpoons Fe$	–0.04
$Pt, H^+/H_2$	$2H^+ + 2e^- \rightleftharpoons H_2$	0.000
$Ag, AgBr/Br^-$	$AgBr + e^- \rightleftharpoons Ag + Br^-$	0.071
$Ag, AgCl/Cl^-$	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	0.222
Normal calomel electrode	$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	0.280
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.344
$Pt/O_2, OH^-$	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	0.400
$Pt/Cr^{3+}, Cr^{2+}$	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	0.410
Pt, quinhydrone, H^+/H_2Q	$Q + 2H^+ + 2e^- \rightleftharpoons H_2Q$	0.699
Hg_2^{2+}/Hg	$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$	0.789
Ag^+/Ag	$Ag^+ + e^- \rightleftharpoons Ag$	0.799
$Pt, Br_2/Br^-$	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.066
$Pt, O_2/H_2O$	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.230
$Pt, Cl_2/Cl^-$	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.329
$Pt/MnO_4^-/Mn^{2+}$	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.520
Au^{3+}/Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	1.500
Pt, Ce^{4+}, Ce^{3+}	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.610
$Pt/Co^{3+}, Co^{2+}$	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.820

15.12 Uses of Standard Potential Values

In Table 15.1 the standard reduction potentials are arranged in the order of increasing potential downwards. The relative values of the potentials of the electrodes as given in the Table (which determine their position in the Table) can be used to predict the relative oxidizing or reducing ability of the electrode system.

Consider the $Zn(s) \mid Zn^{2+}(aq)$ and the $Cu(s) \mid Cu^{2+}(aq)$ electrode systems. The cell (A) is set up as below:

$$Zn(s) \mid Zn^{2+}(aq) \,\|\, Cu^{2+}(aq) \mid Cu(s)$$

$$\begin{aligned} E^{o}_{cell} &= E^{0}_{cathode} - E^{0}_{anode} = \overset{0}{E}_{Cu^{2+}|Cu} - E_{Zn^{2+}|Zn} \\ &= 0.34 - (-0.74) = 1.08 \text{ V} \end{aligned}$$

As the E^{o}_{cell} is positive the reactions that take place are:

At the anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

At the cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Overall reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Again consider the $Ag(s) \mid Ag^{+}(aq)$ and $Cu(s) \mid Cu^{2+}(aq)$ electrode systems. If the cell (B) is set up as below:

$$Ag(s) \mid Ag^{+}(aq) \,\|\, Cu^{2+}(aq) \mid Cu(s)$$

We would consider $Ag(s) \mid Ag^{+}(aq)$ to be the anode and $Cu^{2+}(aq) \mid Cu(s)$ to be the cathode. The electrode reactions would be expected to be as follows:

Anode reaction: $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$

Cathode reaction: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Overall reaction: $2Ag(s) + Cu^{2+}(aq) \rightarrow 2\,Ag^{+}(aq) + Cu(s)$

And the potential of the cell would be

$$\begin{aligned} E^{0}_{cell} &= E^{o}_{cathode} - E^{o}_{anode} = \overset{0}{E}_{Cu^{2+}|Cu} - \overset{0}{E}_{Ag^{+}|Ag} \\ &= 0.34 - (0.80) = -0.46 \text{ V} \end{aligned}$$

The E^{0}_{cell} is negative. Hence the electrode reactions as written do not take place. Rather the reaction will go in the opposite direction so that $Cu^{2+}(aq) \mid Cu(s)$ acts as the anode and the $Ag(s) \mid Ag^{+}(aq)$ as the cathode when the E^{0}_{cell} will be + 0.46 V.

Two important points should be noted:

(a) Whether an electrode reaction is oxidation or reduction, for the purpose of calculation of the cell potential using the equation above reduction potential must always used.

(b) The potential used in the calculation is the value given in the Table and is independent of the number of electron transfer involved.

We can now make some general statements;

In cell A from the Table 15.1, $E^{0}_{Cu^{2+}|Cu}$ is higher than $E^{0}_{Zn^{2+}|Zn}$, so Cu^{2+} ion oxidizes Zn to Zn^{2+} ion. Cu^{2+} ion is a stronger oxidizing agent than Zn^{2+}, i.e. it has greater tendency to get reduced. Again in cell B it is seen that Ag^{+} oxidizes Cu. $Ag^{+}|$ Ag has more positive E° compared to $Cu^{2+}|Cu$ and Ag^{+} ion has a greater tendency to get reduced compared to Cu^{2+}. In general, a species on the left hand side of the list as arranged will have tendency to oxidize a species above it on the right hand side. Cl_2 will oxidize Fe or Cu but will not oxidize Au. All species on the right side are reducing agents. Using similar arguments it can be said that any species on the right hand side of the table will have the tendency to reduce any species below it on the left hand side.

Limitations of the predictions:

A positive value of E^{0}_{cell} for a particular reaction indicates the feasibility of this reaction when the reactants are mixed. It does not necessarily mean that the reaction will take place. Two reasons for such situations are:

(a) The predictions may not be valid if the concentrations are not 1.0 $mol\ L^{-1}$. If, however, with non standard conditions E^{0}_{cell} is positive prediction may be valid.

(b) The reaction may have high activation energy, in which case the rate may be so slow that no reaction will be visible.

Example 15.1: Use the standard potential values in Table 15.1 to determine which of the following species is the strongest oxidizing agent: $Ca^{2+}(aq)$, $Br_2(l)$ and MnO_4^- (in acid solution).

Solution: The strongest oxidizing agent is the one which has the highest standard reduction potential. From the Table we see that

$$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s) \qquad E^{0}_{red} = -2.87\ \text{V}$$

$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \qquad E^{0}_{red} = 1.09\ \text{V}$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^{0}_{red} = 1.52\ \text{V}$$

Since MnO_4^-/Mn^{2+} has the highest positive potential MnO_4^- is the strongest oxidizing agent

Example 15.2: Use standard potential values from the Table to predict if the following reaction will take place or not:

$$3Fe^{2+}(aq) + 2Al(s) \rightarrow 2Al^{3+}(aq) + 3Fe(s)$$

***Solution*:** The reduction reaction: $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ Cathode

The oxidation reaction: $Al(s) \rightleftharpoons Al^{3+}(aq) + 3e^-$ Anode

When a cell is set up in which this reaction takes place the standard potential of the cell is given by

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = -0.44 - (-1.66) = 1.22\text{ V}$$

Since the potential of the cell is positive the reaction as written will take place.

Example 15.3: Use standard potential values to predict if the following reaction is feasible or not under standard conditions:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Cl^-(aq) \rightarrow 2Cr^{3+}(aq) + 3Cl_2(g) + 7H_2O(l)$$

Solution: When a cell is set up

The anode reaction: $2Cl^-(aq) \rightleftharpoons Cl_2(g) + 2e^-$

The cathode reaction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 1.33 - 1.36 = -0.03\text{ V}$$

As the value of E^o_{cell} is negative the reaction is not feasible under standard conditions.

15.13 Effect of Concentration and Temperature on Electrode Potential: The Nernst Equation

So far the discussion has been confined to standard electrodes, i.e. when the concentration of the ion is 1.0 $mol\ L^{-1}$, and their potentials. In 1889 Nernst pointed out that electrode potentials are dependent on concentration and temperature, and for the electrode reaction

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

he derived the following equation giving this dependence:

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}] \tag{15.11}$$

For a general form of the electrode reaction

$$\text{Oxidised form} + ne^- \rightleftharpoons \text{Reduced form}$$

the Nernst equation takes the form

$$E = E^o - \frac{RT}{nF} \ln \frac{c_{(reduced\ form)}}{c_{(oxidized\ form)}} \tag{15.12}$$

[***Note:*** *In electrolytic systems activity (a) rather than concentration (c) is generally used, because in non-ideal systems activity is considered as the 'effective' concentration. However, in this text we will use concentration term in deriving relationship between concentration and potential and in explaining related phenomenon.*]

As has been stated earlier, E^o is the standard potential, R is the universal gas constant in joules $K^{-1}mol^{-1}$, T is temperature in Kelvin, F is the Faraday constant, n is the number of electrons transferred in the electrode half–reaction and ln is the logarithm to the base e. In equation (15.1) M^{n+} is the oxidized form and M is the reduced form of the metal M. For this electrode the Nernst equation (15.11) takes the form

$$E = E^0_{M^{n+}|M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \tag{15.13}$$

Since the concentration of solid metal is taken as unity equation (15.13) reduces to

$$E = E^o + \frac{RT}{nF} \ln [M^{n+}] \tag{15.14}$$

Examples of the forms of Nernst equation for different electrodes deduced from equation (15.11) are given below:

(a) For the $Zn^{2+}|Zn$ electrode at temperature of 25°C electrode potential at concentrations other than 1.0 $mol\ L^{-1}$

$$\begin{aligned} E_{Zn^{2+}|Zn} &= E^0_{Zn^{2+}|Zn} + \frac{2.303 \times 8.316 \times 298}{96500\ n} \log [Zn^{2+}] \\ &= E^0_{Zn^{2+}|Zn} + \frac{0.0591}{1} \log [Zn^{2+}] \end{aligned}$$

(b) For $Ag^+|Ag$ electrode, according to Nernst

$$E_{Ag^+|Ag} = E^0_{Ag^+|Ag} + \frac{0.059}{1} \log [Ag^+]$$

(c) For a $Ag,AgCl(s)|Cl^-(aq)$ electrode reaction is $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$ and Nernst equation for this electrode is

$$\begin{aligned} E &= E^0_{AgCl|Cl^-} - \frac{RT}{nF} \ln \frac{[Ag]\,[Cl^-]}{[AgCl]} = E^0_{AgCl|Cl^-} - \frac{0.0591}{1} \log [Cl^-] \\ &= E^0_{AgCl|Cl^-} - (0.0591) \log [Cl^-] \end{aligned}$$

(d) For a $Pt|\ Cl_2(g),Cl^-(aq)$ the electrode reaction is $Cl_2(g) + 2e^- \rightleftharpoons 2\,Cl^-(aq)$ and the Nernst equation is

$$\begin{aligned} E &= E^0_{Cl_2|Cl^-} - \frac{RT}{nF} \ln \frac{[Cl^-]^2}{[Cl_2(g)]} = E^0_{Cl_2|Cl^-} - \frac{0.0591}{2} \log [Cl^-]^2 \\ &= E^0_{Cl_2|Cl^-} - (0.0591) \log [Cl^-] \end{aligned}$$

since $n = 2$ from the equation and $[Cl_2(g)]$ is taken as unity.

This indicates that potential of an electrode which is reversible with respect to a cation under non-standard conditions increases when the concentration of the metal ions increases but it decreases when the concentration decreases. When the electrode is reversible with respect to the anion the potential decreases with increase of the concentration of the anion and increases with decrease of the ion concentration.

(e) When an electrode reaction involves a cation in different oxidation states as in the case of $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ Nernst equation takes the form

$$E_{Fe^{2+}|Fe^{3+}} = E^0_{Fe^{2+}|Fe^{3+}} - \frac{RT}{nF} ln \frac{c_{(reduced\ form)}}{c_{(oxidized\ form)}} \qquad (15.15)$$

At 298K

$$E_{Fe^{2+}|Fe^{3+}} = E^0_{Fe^{2+}|Fe^{3+}} - \frac{0.0591}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

It may be noted that when $[Fe^{2+}] = [Fe^{3+}]$, $E_{Fe^{2+}|Fe^{3+}} = E^0_{Fe^{2+}|Fe^{3+}}$

Some applications of these equations are shown below:

Example 15.4: Calculate the electrode potential of the $Zn^{2+}|\ Zn$ electrode when the concentration of the Zn^{2+} ions is 0.20 mol L^{-1}

Solution:

$$\begin{aligned} E_{Zn^{2+}/Zn} &= E^0_{Zn^{2+}/Zn} + \log [Zn^{2+}] \\ &= -0.76 + \frac{0.0591}{2} \log (0.02) \\ &= -0.76 + (0.02955)(-1.70) \\ &= -0.810 \text{ V} \end{aligned}$$

Example 15.5: Calculate the potential of $Ag^+|\ Ag$ electrode when a rod of Ag is dipped into a solution of $AgNO_3$ of concentration 1.30 $mol\ L^{-1}$.

Solution:

$$\begin{aligned} E_{Ag^+/Ag} &= E^0_{Ag^+/Ag} + \frac{0.0591}{1} \log [Ag^+] \\ &= 0.80 + 0.0591 \log 1.3 \\ &= 0.800 + (0.0591)(0.112) \\ &= 0.807 \text{ V} \end{aligned}$$

The reduction potentials calculated with the help of the Nernst equation can be used to calculate the potential of the cell.

***Example 15.6*:** Calculate the potential at 25°C of the cell

$$Sn|Sn^{2+}\ (0.10\ mol\ L^{-1})\ ||\ Fe^{3+}\ (0.30\ mol\ L^{-1})\ |\ Fe$$

Solution: The reaction taking place in the cell will be

$$3Sn(s) + 2\ Fe^{3+}\ (aq) \rightleftharpoons 3\ Sn^{2+}\ (aq) + 2\ Fe(s)$$

The electrode reactions are

At left electrode: $Sn \rightleftharpoons Sn^{2+} + 2e^-$

At right electrode: $Fe^{3+} + 3e^- \rightleftharpoons Fe$

$$E_{cell} = E_{cathode} - E_{anode} = E_{Fe^{3+}/Fe} - E_{Sn^{2+}/Sn}$$

$$= \left\{E^0_{Fe^{3+}/Fe} + \frac{0.0591}{3}\log(0.3)\right\} - \left\{E^0_{Sn^{2+}/Sn} + \frac{0.0591}{2}\log(0.10)\right\}$$

$$= \{-0.036 + \frac{0.0591}{3}\log(0.3)\} - \{(-0.140 + \frac{0.0591}{2}\log(0.10)\}$$

$$= -0.036 + (0.0197)(-0.525) - \{(-0.140 + (0.02995)(-1.0)\}$$

$$= -0.026 - 0.170$$

$$= -0.196\text{ V}$$

Since the potential of the cell is negative the reaction as written will not be spontaneous. The opposite reaction will be spontaneous.

Example 15.7: Calculate the *e.m.f.* of the cell

$$Ag, AgCl(s) \mid Cl^-(0.050\ mol\ L^{-1}) \parallel Fe^{3+}\ (0.10\ mol\ L^{-1}) \mid Fe^{2+}\ (0.02\ mol\ L^{-1}) \mid Pt$$

Solution: The electrode reactions are

At left electrode: $Ag + Cl^- \rightleftharpoons AgCl + e^-$

At right electrode: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$E_{left} = E^0_{left} - \frac{0.0591}{1}\log[Cl^-]$$

$$= 0.2225 - (0.0591)\log 0.05$$

$$= 0.2225 + 0.0769 = 0.2994\text{ V}$$

$$E_{right} = E^0_{right} - (0.0591)\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771 - 0.0591\log(0.02)/(0.01)$$

$$= 0.771 - 0.0177 = 0.7533\text{ V}$$

Finally, the cell *e.m.f.* is

$$E_{cell} = E_{right} - E_{left}$$

$$= +0.7533 - 0.2994$$

$$= +0.4539 = 0.454\text{ V}$$

15.14 Determination of pH of a Solution

The change of potential with change in concentration of ions has been used in chemistry in many ways. Like all other electrodes, the potential of a hydrogen electrode which is reversible with respect to hydrogen ions changes with change in the concentration of H^+ ions in accordance with the Nernst equation. Based on this fact methods have been devised to determine the *pH* of a solution from measurements of potentials of electrochemical cells. For this purpose a cell is set up with a standard electrode and an electrode containing the solution whose *pH* is to be measured. The standard electrode used for these measurements is usually a calomel electrode. The cell can be written as

$$Pt \mid H_2(1atm) \mid H^+ \,(c_{H^+}\; 1.0\ mol\ L^{-1}) \,\|\, Cl^- \,(1.0\ mol\ L^{-1}) \mid Hg_2Cl_2(s) \mid Hg$$

Using the Nernst equation the *e.m.f*, of the cell at 25°C can be expressed as

$$E_{cell} = E_R - E_L = E_{calomel} - E_{H^+/H_2}$$

$$E_{cell} = E_{calomel} - \left(E^0_{H^+/H_2} + \frac{0.0591}{2} \log\,[H^+]^2\right)$$

As at the hydrogen electrode the reaction taking place is

$$2H^+ + e \rightleftharpoons H_2$$

But $$E^0_{H^+/H_2} = 0.0\text{ V}$$

Hence, $$E_{cell} = E_{calomel} - 0.0591 \log\,[H^+]$$
$$= E_{calomel} + (0.0591)\,pH$$

Or $$(E_{cell} - E_{calomel}) = (0.0591)\,pH$$

Therefore $$pH = \frac{E_{cell} - E_{calomel}}{0.0591} \qquad (15.16)$$

Example 15.3: The *e.m.f.* of the following cell at 25°C is 0.400V

$$Pt \mid H_2(1atm) \mid H^+ \,(c_{H^+}\; 1.0\ mol\ L^{-1}) \,\|\, Cl^- \,(1.0\ mol\ L^{-1}) \mid Hg_2Cl_2(s) \mid Hg$$

Given that the $E^0_{calomel} = 0.2812$ V, calculate the *pH* of the solution.

Solution: Substituting in the equation (15.16)

$$pH = \frac{0.400 - 0.2812}{0.0591} = 2.01$$

5.14.1 Glass electrode: the pH meter

At the present time in most applications *pH* is measured with the help of a glass electrode coupled with a standard calomel electrode.

A glass electrode (Figure 15.9) consists of a silver wire coated with silver chloride immersed in a solution of hydrochloric acid solution of constant *pH* (buffer solution) and placed inside a container made of special glass. The potential of the glass electrode is found to change with the hydrogen ion concentration of the solution in which it is immersed, i.e. it is reversible with respect to the H^+ ions. Using Nernst equation for the electrode reaction at the glass electrode

$$2H^+(aq) + 2e \rightarrow H_2(g)$$

the potential of this glass electrode is given by

$$\begin{aligned} E_{glass} &= E^0_{glass} - \frac{0.0591}{2} \log \frac{[H_2(g)]}{[H^+]^2} \\ &= E^0_{glass} + (0.0591) \log [H^+] \\ &= E^0_{glass} - (-0.0591) \log [H^+] \\ &= E^0_{glass} - 0.0591\, pH \qquad (15.17) \end{aligned}$$

In order to determine the *pH* of an unknown solution the glass electrode and the calomel electrode both are dipped in the solution to set up the following cell:

Glass electrode | Solution of unknown *pH* | Calomel electrode

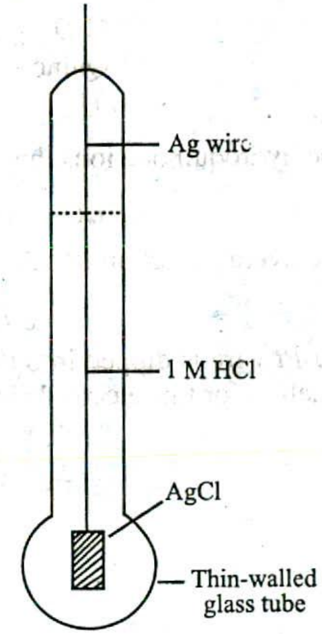


Figure 15.9 Glass Eelectrode

The *e.m.f.* of the cell is given by

$$E_{cell} = E_{calomel} - E_{glass} \qquad (15.18)$$

Substituting equation (15.17) into (15.18) we get

$$E_{cell} = E_{calomel} - (E^0_{glass} - 0.0591\, pH) \qquad (15.19)$$

$$pH = \frac{E_{cell} - E_{calomel} + E_{glass}}{0.0591} \qquad (15.20)$$

Thus the *pH* of an unknown solution can be easily determined by measuring the *e.m.f.* of the cell, since $E_{calomel}$ *and* E^0_{glass} (E^o_{glass} can be determined by using a solution of known *pH* in the above cell) are known. In fact in commercial *pH* meters the potential values are converted into *pH* values which are directly read from the dial of the instrument.

Glass electrodes are commercially available as these are simple to use and are not affected by oxidizing and reducing agents.

15.14.2 The Quinhydrone electrode

pH meters are expensive instruments and glass electrodes are fragile. A convenient and much less expensive electrode for measuring pH of solutions can be prepared by using quinhydrone. Quinhydrone (*Q*) is an equimolar mixture of hydroquinone (H_2Q) and quinone (*Q*). Both are sparingly soluble in water. When dissolved in water quinone is reduced to hydroquinone ions,

$$\underset{\substack{\text{Quinone}\\ Q}}{C_6H_4O_2\ (aq)} + 2e^- \rightarrow \underset{\substack{\text{Hydroquinone ion}\\ H_2Q}}{C_6H_4O_2^{2-}\ (aq)}$$

The hydroquinone ions then combine reversibly with H$^+$ ions to form quinone.

$$C_6H_4O_2^{2-}\ (aq) + 2H^+\ (aq) \rightleftharpoons C_6H_6O_2\ (aq)$$

The overall reaction is then

$$C_6H_6O_2\ (aq) \rightleftharpoons C_6H_4O_2(aq) + 2H^+(aq) + 2e^-$$

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

$$\begin{aligned}
E_{Q/H_2Q} &= E^0_{Q/H_2Q} - \frac{RT}{2F}\ ln\frac{[H_2Q]}{[Q]\,[H^+]^2}\\
&= E^0_{Q/H_2Q} - \frac{RT}{2F}\ ln\frac{1}{[H^+]^2},\ \text{since}\ \frac{[H_2Q]}{[Q]} = 1\\
&= E^0_{Q/H_2Q} + \frac{RT}{F}\ ln\ [H^+]\\
&= E^0_{Q/H_2Q} + 0.0591\ log_{10}\ [H^+] \quad (\text{at } 298\ \text{K})\\
&= 0.6996 - 0.0591\ pH \qquad (15.21)
\end{aligned}$$

where $E^0_{Q/H_2Q} = 0.6996$ V

In order to determine the *pH* of an unknown solution the following cell is set up:

$$Hg\ |\ Hg_2Cl_2(s)\ |\ KCl(satd.)\ ||\ H^+(test\ solution)\ |\ Q\ |\ H_2Q\ |\ Pt$$

The *e.m.f* of this cell is given by

$$\begin{aligned}
E_{cell} &= E_R - E_L\\
&= (0.6996 - 0.0591\ pH) - E_{calomel}
\end{aligned}$$

$$(0.6996 - 0.0591\ pH) = E_{cell} + E_{calomel}$$

Therefore,

$$pH = \frac{0.6996 - E_{cell} - E_{calomel}}{0.0591} \qquad (15.22)$$

Thus the *pH* of an unknown solution can be determined.

15.15 Thermodynamics and E.M.F. of Cells

Principles of thermodynamics can be applied to different aspects of electrode and cell potentials, like derivation of the free energy change, Nernst equation for the dependence of electrode potential on concentration and temperature, calculation of equilibrium constants and enthalpy change of red-ox reactions. These will be seen below:

15.15.1 Electrical work and energy: free energy of reactions

We know that in a Galvanic cell chemical energy is converted into electrical energy and is capable of doing useful work. Thermodynamic principle can be applied to derive useful relationship between cell potential and maximum amount of work ($W_{ele,\,\max}$) that can be obtained from a cell reaction. The electrical energy is given by,

$$Energy = Q\,E_{cell} = I\,t\,E_{cell} = Coulomb \times Volt = Joule \qquad (15.23)$$

$$(1\ \mathrm{J} = 1\ \mathrm{C} \times 1\ \mathrm{V})$$

Here, $Q\ (= It)$ is the total electrical charge in coulomb passed through the cell, E_{cell} is the electrical potential in volt, or *e.m.f* of the cell, I is the current in ampere and t is the time in seconds.

When n moles of electrons are transferred during a cell reaction the total charge carried is

$$\mathrm{Q} = nF \qquad (15.24)$$

F is the Faraday constant ($1F = 96500\ \mathrm{C/mol}$). From equations (15.23) and (15.24)

$$Energy = -\ nFE_{cell} \qquad (15.25)$$

Now, the maximum amount of electrical energy that can be obtained from any chemical reaction is equal to the maximum electrical work ($W_{ele,\max}$). Therefore,

$$W_{ele,\max} = -nFE_{cell} \qquad (15.26)$$

The negative sign on the right-hand side of equation (15.26) and equation (15.25) indicates that $W_{ele,\max}$ is done by the system on the surrounding.

In *(Section 7.12.1)* the change of free energy *(ΔG)* was defined as the energy available to do work, e.g., $\Delta G = W_{max}$. Therefore, equation (15.26) can be written as,

$$\Delta G = W_{ele,\max} = -nFE_{cell} \qquad (15.27)$$

In equation (15.27) both n and F are positive quantities and *for a spontaneous cell reaction ΔG is negative. This, of course, implies that E_{cell} must be positive for a cell reaction to occur spontaneously.*

If the concentration of the components of the cell is 1.0 $mol\ L^{-1}$ at standard temperature $E_{cell} = E^0_{cell}$ and if the cell operates reversibly, we can write,

$$\Delta G^0 = -nFE^0_{cell} \qquad (15.28)$$

Equation (15.28) allows us to calculate ΔG^0 and any other thermodynamic quantities that can be obtained from ΔG^0 for any reaction for which E^0_{cell} is measured.

Example 15.9: For a cell write down the half- reactions, net cell reaction and cell potential if the two electrodes are $Fe^{2+} \mid Fe$ and $Ni^{2+} \mid Ni$. Calculate the ΔG^0 for the cell reaction.

Solution: From Table 15.1, the standard reduction potentials of $Fe^{2+} \mid Fe$ and $Ni^{2+} \mid Ni$ electrodes are – 0.440 and – 0.250 V respectively:

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \qquad E^0_{Fe^{2+}|Fe} = -0.440 \text{ V}$$

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E^0_{Ni^{2+}|Ni} = -0.250 \text{ V}$$

Since $E^0_{Ni^{2+}|Ni}$ is less negative than $E^0_{Fe^{2+}|Fe}$ in the cell, $Ni^{2+} \mid Ni$ electrode will be the cathode and the other electrode will be the anode. Hence the standard *e.m.f.* of the cell in which the following reaction takes place

$$Ni^{2+}(aq) + Fe(s) \rightleftharpoons Ni(s) + Fe^{2+}(aq)$$

is given by

$$\begin{aligned} E^0_{cell} &= E^0_{Ni^{2+}|Ni} - E^0_{Fe^{2+}|Fe} \\ &= -0.250 - (-0.440) \\ &= +0.190 \text{ V}. \end{aligned}$$

ΔG^0 can be calculated from equation (15.28). Here, $n = 2$

Hence
$$\begin{aligned} \Delta G^0 &= -nF\,E^0_{cell} = -(2) \times (96,500) \times (0.190) \\ &= -3.67 \times 10^4 \text{ J} \end{aligned}$$

15.15.2 Derivation of the Nernst equation

Let us consider the general reaction,

$$aA + bB \rightleftharpoons mM + nN$$

From equation (10.33) we can write

$$\Delta G = \Delta G^0 + RT \ln Q \qquad (15.29)$$

where $Q = \dfrac{a_M^m \times a_N^n}{a_A^a \times a_B^b}$ is the reaction quotient of the reaction This is an exact thermodynamic relationship. Here a represents the activity of the species in equilibrium, R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature in K.

We have seen that $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$. Therefore, equation (15.29) can be written as

$$-nFE = -nFE^0 + RT\,In\,Q \qquad (15.30)$$

Dividing equation (15.30) by $-nF$ we get

$$E = E^0 - \frac{RT}{nF}RT\,In\,Q \qquad (15.31)$$

For an electrode $M^{n+} \mid M$ in which the reaction is

$$M^{n+} + ne^- \rightleftharpoons M$$

we can write $$Q = \frac{[M]}{[M^{n+}]}$$

so that $$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

Since $[M] = 1$, $$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

Or, $$E_{M^{n+}/M} = E^0_{M^{n+}/M} + \frac{RT}{nF}\ln\,[M^{n+}]$$

This is the same as the one (equation (15.4) derived by Nernst for the dependence of electrode potential on concentration and temperature.

The dependence of the potential of a cell on the concentration of the ions at the cathode and anode side can be derived just by writing the Nernst equation for the two electrodes in the relation

$$E_{cell} = E_{cathode} - E_{anode}$$

15.15.3 Calculation of equilibrium constant of a red-ox reaction

The equilibrium constant of a red-ox reaction can be related to E^0_{cell}. We have seen (*Section 10.14*) that the ΔG^0 of a reversible reaction is related to the equilibrium constant K_{eq} as follows:

$$\Delta G^0 = -RT\ln K_{eq}$$

Therefore, from equations (15.28) we can write

$$-nF\,E^0_{cell} = -RT\ln K_{eq} \qquad (15.32)$$

Solving for $\ln K_{eq}$ we find

or $$\ln K_{eq} = \frac{nFE^0_{cell}}{RT} \qquad (15.33)$$

Equation (15.33) can be written as $$2.303\log K_{eq} = \frac{nFE^0_{cell}}{RT} \qquad (15.34)$$

At $T = 298$ K, equation (15.34) can be written as,

$$\log K_{eq} = \frac{n(96500)E^0_{cell}}{(8.314)(298)(2.303)} \qquad (15.35)$$

$$= \frac{nE^0_{cell}}{0.0591} \qquad (15.36)$$

Thus the equilibrium constant of a red-ox reaction can be calculated if the E^0_{cell} is determined. This is illustrated in the following examples.

Example 15.10: Calculate the equilibrium constant of the reaction,

$$Zn(s) + Sn^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Sn(s)$$

Solution: The standard reduction potentials of the Zn and Sn electrodes (Table 15.1) indicate that $E^0_{Zn^{2+}/Zn}$ electrode is more negative than $E^0_{Sn^{2+}/Sn}$ electrode. So Zn electrode is anode (L) and Sn electrode is cathode (R). Therefore,

$$\begin{aligned} E^0_{cell} &= E^0_{Sn^{2+}/Sn} - E^0_{Zn^{2+}/Zn} \\ &= -0.136 - (-0.763) \\ &= 0.627 \text{ V} \end{aligned}$$

From equation (15.36) we find

$$\log K_{eq} = \frac{2}{0.0591} \times 0.627 = 21.18$$

Or, $K_{eq} = 1.51 \times 10^{21}$

Example 15.11: Calculate the equilibrium constant of the following reaction at 298 K.

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

Solution: The standard reduction potentials of $Zn^{2+}|Zn$ and $Cu^{2+}|Cu$ electrodes are -0.763 and 0.337 V respectively. Hence the $Cu^{2+}|Cu$ electrode is the cathode (it has higher value of E^o) and $Zn^{2+}|Zn$ electrode is the anode, and

$$\begin{aligned} E^0_{cell} &= E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} \\ &= 0.337 - (-0.763) \\ &= 1.10 \text{ V} \end{aligned}$$

Using equation (15.36) $\log K_{eq} = \dfrac{2 \times 1.10}{0.0591}$

$$= 37.225$$

Hence $K_{eq} = 1.69 \times 10^{37}$

We see that when zinc is dipped into a solution of Cu^{2+} practically all of Cu will be deposited.

Example 15.12: Calculate from *e.m.f.* data the equilibrium constant for the reaction taking place at 25°C in the cell

$$Zn|\ Zn^{2+}\ (1.0\ mol\ L^{-1})\ \|\ Fe^{3+}\ (1.0\ mol\ L^{-1}),\ Fe^{2+}\ (1.0\ \ mol\ L^{-1}\ )|\ Pt$$

Solution: The half-cell reactions are

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^{-} \qquad E^{0}_{red} = -0.763$$

$$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq) \qquad E^{0}_{red} = +0.771$$

Overall reaction: $Zn(s) + 2F^{3+}(aq) \rightleftharpoons Zn^{2+}(aq) + 2Fe^{2+}(aq)$

$$\begin{aligned} E^{0}_{cell} &= E^{0}_{right} - E^{0}_{left} \\ &= +0.771 - (-0.763) \\ &= 1.534\ \text{V} \end{aligned}$$

Using equation (15.36) $\log K_{eq} = \dfrac{2\times1.534}{0.0591} = 51.91$

or $K_{eq} = 8.12 \times 10^{51}$

This indicates that when Zn is added to a solution Fe^{3+} ion practically all of the Fe^{3+} ions will be reduced to the Fe^{2+} state.

15.15.4 Determination of enthalpy of reaction

Equation (15.27) together with Gibbs-Helmholtz equation (*Section 7.13*) yields other valuable information. The Gibbs-Helmholtz equation is

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)$$

Differentiation of equation (15.27) with respect to temperature at constant pressure yields

$$\frac{\partial(\Delta G)}{\partial T} = -nF\left(\frac{\partial E}{\partial T}\right)_P \tag{15.37}$$

Here $\left(\dfrac{\partial E}{\partial T}\right)_P$ represents the rate of change of *e.m.f.* with temperature or the temperature co-efficient of *e.m.f.* Substitution of equations (15.37) and (15.27) into the Gibbs-Helmholtz equation (7.75) gives,

$$-n\,F\,E = \Delta H - n\,F\,T\left(\frac{\partial E}{\partial T}\right)_P \tag{15.38}$$

This can be rearranged to write

$$\Delta H = -n\,F\,E + n\,F\,T\left(\frac{\partial E}{\partial T}\right)_P \tag{15.39}$$

From equation (15.39) it is evident that the enthalpy of reaction taking place in the cell may be obtained from the value of the *e.m.f.* and the temperature co-efficient of the *e.m.f.* Equation (15.38) can also be written as

$$nFE = -\Delta H + nFT\left(\frac{\partial E}{\partial T}\right)_P \qquad (15.40)$$

It can be deduced from equation (15.40) that the electrical energy nFE can have a value equal to, greater or less than the enthalpy of reaction depending on the temperature co-efficient, $\left(\frac{\partial E}{\partial T}\right)_P$. Let us consider these cases:

Case 1: When $\left(\frac{\partial E}{\partial T}\right)_P = 0, \qquad nFE = -\Delta H$

In other words, the electrical energy produced is equal to the enthalpy change.

Case 2: When $\left(\frac{\partial E}{\partial T}\right)_P$ is positive, i.e., $\left(\frac{\partial E}{\partial T}\right)_P > 0$ and $nFE > (-\Delta H)$

Accordingly, the electrical energy produced is greater than the enthalpy of reaction at constant pressure.

Case 3: When $\left(\frac{\partial E}{\partial T}\right)_P$ is negative, i.e., $\left(\frac{\partial E}{\partial T}\right)_P < 0$ and $nFE < (-\Delta H)$

In this case, the electrical energy produced is less than the enthalpy of reaction at constant pressure. The calculation of ΔH from the measurement of E is demonstrated in the following examples.

Example 15.13: At 298 K the *e.m.f.* of the reversible cell

$$Pb \mid PbCl_2(s) \mid KCl(aq) \mid AgCl(s) \mid Ag$$

is 0.4902 V and $\left(\frac{\partial E}{\partial T}\right)_P = -1.86 \times 10^{-4}$ V deg^{-1}. Calculate the values of ΔG and ΔH in joules if the cell reaction is $Pb + 2AgCl = PbCl_2 + 2Ag$

Solution:

$$\begin{aligned} \Delta G &= -n\,F\,E \\ &= -2\,(96{,}500)\,(0.4902) \\ &= -94{,}500 \end{aligned}$$

$$\text{and } \Delta H = -n\,F\,E + n\,F\,T\left(\frac{\partial E}{\partial T}\right)_P$$

$$\begin{aligned} &= -2\,(96{,}500)\,(0.4902) + 2\,(96{,}500)\,(298)\,(-1.86 \times 10^{-4})\ J \\ &= -101{,}600\ J \end{aligned}$$

The value of ΔH obtained from *e.m.f.* measurements is in excellent agreement with the value obtained calorimetrically for this and many other reactions.

15.16 Liquid Junction Potential: Salt Bridge

If in a cell two electrolytic solutions or two solutions of the same electrolyte but of different concentrations, are in contact then a potential difference is usually developed across the boundary between the two solutions. Such potential is called the *liquid junction potential.* This arises due to the unequal velocities of the ions in contact. Consider the boundary

$$HCl(c_1)|HCl(c_2)$$

where $c_1 < c_2$ and the vertical line indicating that the liquids are in contact. The hydrogen ions and chloride ions tend to diffuse into the more dilute solution, but the H^+ ions diffuse more rapidly than the Cl^- ions. As a result the dilute solution becomes positively charged while the concentrated solution is negatively charged. This separation of charges gives rise to a potential difference across the boundary and slows down the faster moving ion and speeds up the slower moving ion. A steady state is eventually reached when the two ions migrate with the same speed.

For accurate measurements of potentials of cells liquid junction potential should be eliminated as far as practicable. The most convenient way of minimizing the junction potential is to use a salt bridge prepared with solution of saturated potassium chloride or ammonium nitrate or potassium nitrate set in agar jelly (*Section15.7*). As shown, a doubly bent tube is filled with the jelly containing the salts, the two ends of the tube being placed in two separate electrode vessels. This introduces two liquid junctions, but as the ion pairs given by the above mentioned salts have almost equal transport numbers and these ions are present in overwhelmingly large numbers at the boundaries the effect of the other ions tends to be swamped out. Of the three salts mentioned potassium chloride is to be preferred where this can be used.

15.17 Types of Galvanic Cell

In a typical electrochemical cell the cell potential is a direct consequence of the net chemical reaction. There may be another type of galvanic cell in which the chemical reaction is secondary, and the cell potential is a consequence of differences in concentration of either of the *electrodes* or of the *electrolytic solution.* These types of cells are called *concentration* cells. When the difference is in the concentration of electrodes, the cell is called *electrode concentration* cell. On the other hand if the potential arises due to the difference in the concentration of electrolyte, the cell is known as *electrolytic concentration cell.* There may be four different categories of galvanic cells.

(1) Electrochemical cell without transference
(2) Electrochemical cell with transference
(3) Concentration cell without transference
(4) Concentration cell with transference

Type 1 cell: In this type of cell, the two electrodes are immersed in two electrolytic solutions separated by a salt bridge to avoid liquid junction potential. Daniel cell is an example of this type of cell. We have already discussed this type of cells.

Type 2 cell: In this case no salt bridge is used. There is a phase boundary in the form of a porous diaphragm and the ions move at different speeds through the liquid junction. This results in a junction potential, E_j. An example is

$$Sn(s) \mid Sn^{2+}(aq) \mid Cu^{2+}(aq) \mid Cu(s)$$

The cell potential will also include junction potential E_j.

Type 3 cell: As already mentioned, the concentration cell without transference may be of two types: (i) *electrode concentration* cells and (ii) *electrolytic concentration cells.*

(i) *Electrode concentration cells (without transference):* This type of cell depends on the difference in concentrations at the electrodes. This may again be of two types:

(a) *Gas electrode:* Two gas electrodes immersed in the same solution of the ions of the gaseous element, but the gas bubbled around the electrodes have different pressures. Examples are

$$Pt| Cl_2(g, p_{Cl_2} = P_1\, atm) \mid Cl^-(aq) \mid Cl_2(g, p_{Cl_2} = P_2\, atm) \mid Pt$$

$$Pt| H_2(g, p_{H_2} = P_1\, atm) \mid H^+(aq) \mid H_2(g, p_{H_2} = P_2\, atm) \mid Pt$$

As can be seen, there is no transfer of electrolyte in this case.

(b) *Amalgam electrode:* In this case the amount of metal mixed with mercury is different. A typical cell diagram is

$$Na(Hg)(c_{Na})_A \mid Na^+(aq) \mid Na(Hg)(c_{Na,})_B$$

(ii) *Electrolytic concentration cells (without transference):* Two similar electrodes are immersed into two electrolytic solutions of different concentrations. The electrolytes are separated by a salt bridge.

$$Pt \mid H_2\,(1\ atm) \mid H^+\,(c_1) \parallel H^+\,(c_2) \mid H_2\,(1\ atm) \mid Pt$$

Here both the electrodes are hydrogen electrodes, and at each electrode the H_2 gas at 1 atm pressure is passed. The concentrations of the H^+ ions are different in the two electrodes compartments. Let us consider another example,

$$Zn(s) \mid Zn^{2+}\,(c_1) \parallel Zn^{2+}\,(c_2) \mid Zn(s)$$

Here also both the electrodes are same, but in one the concentration of Zn^{2+} ions is c_1 and in another it is c_2. There is no phase boundary and the electrolytes are separated by a salt bridge.

Type 4 cell: In this type of cells, the two electrodes are same but the concentrations of the electrolytes are different, and the two electrolytic solutions are placed in direct contact. There is no salt bridge between them. Three examples of this type are

$$Pt \mid H_2\,(1\ atm),\, H^+\,(c_1) : H^+\,(c_2),\, H_2\,(1\ atm) \mid Pt$$

$$Zn(s) \mid Zn^{2+}\,(c_1) : Zn^{2+}\,(c_2) \mid Zn(s)$$

The dotted line is indicative of phase boundary between the two electrolytes having different concentrations. Since the two electrolytes are in direct contact there will be a liquid junction. In this type of concentration cell there is a direct transfer of electrolyte from one solution to the other solution.

15.17.1 E.M.F. of electrode concentration cell without transference

Let us consider the electrode concentration cell consisting of two hydrogen gas electrodes.

$$\text{Pt} \mid H_2\,(g, P_{H_2} = P_1) \mid H^+(aq) \mid H_2(g, P_{H_2} = P_2) \mid \text{Pt}$$

Reaction at the anode, i.e., at the left hand electrode:

$$\frac{1}{2}H_2(P_1) \rightarrow H^+(c_{H^+}) + e^- \tag{15.41}$$

In order to write Nernst equation for the reaction (15.41) we need to write this reaction in the reduction form,

$$H^+(c_{H^+}) + e^- \rightarrow \frac{1}{2}H_2(P_1) \tag{15.41a}$$

Reduction potential of this electrode according to Nernst is

$$E_L = E^0_{H^+,H_2} - \frac{RT}{F}\,ln\frac{P_1^{\frac{1}{2}}}{c_{H^+}} \tag{15.42}$$

$$\text{or} \qquad E_L = -\frac{RT}{F}\,ln\frac{P_1^{\frac{1}{2}}}{c_{H^+}}, \quad \text{since } E^0_{H^+,H_2} = 0 \tag{15.43}$$

Reaction at the cathode, i.e., at the right hand electrode:

$$H^+(c_{H^+}) + e^- \rightarrow \frac{1}{2}H_2(P_2) \tag{15.44}$$

Reduction potential of this electrode according to Nernst:

$$E_R = E^0_{H^+,H_2} - \frac{RT}{F}\,ln\frac{P_2^{\frac{1}{2}}}{c_{H^+}} \tag{15.45}$$

$$\text{or} \qquad E_R = -\frac{RT}{F}\,ln\,\frac{P_2^{\frac{1}{2}}}{c_{H^+}} \tag{15.46}$$

The overall cell reaction is obtained by subtracting equations (15.43) from (15.46). The cell potential is

$$E_{cell} = E_R - E_L \tag{15.47}$$

$$= -\frac{RT}{F}\,ln\,\frac{P_2^{\frac{1}{2}}}{c_{H^+}} - \left\{-\frac{RT}{F}\,ln\,\frac{P_1^{\frac{1}{2}}}{c_{H^+}}\right\} \tag{15.48}$$

$$= \frac{RT}{F}(\,lnP_1^{\frac{1}{2}} - ln\,c_{H^+}) - \frac{RT}{F}(ln\,P_2^{\frac{1}{2}} - ln\,c_{H^+}) \tag{15.48a}$$

Equation (15.48a) upon rearrangement and canceling the common terms turns into

$$E_{cell} = \frac{RT}{2F} ln \frac{P_1}{P_2} \tag{15.49}$$

It is significant to note from equation (15.49) that the *e.m.f* of the cell is entirely dependent on the pressures P_1 and P_2 and in no way dependent on the concentration of the H^+ ions, and there is no transference of electrolyte.

Similarly an expression $E_{cell} = \frac{RT}{2F} ln \frac{c_1}{c_2}$ can be derived for the *e.m.f* of electrode concentration cell without transference consisting of amalgam electrodes, e.g.

$$Na(Hg)(c_{Na} = c_1) \mid Na^+(aq) \mid Na(Hg)\ (c_{Na} = c_2)$$

15.17.2 E.M.F. of electrolyte concentration cell without transference

Let us consider a concentration cell with different concentrations of the H^+ ions at the two electrodes.

$$Pt \mid H_2(1\,atm), H^+(c_1) \parallel H^+(c_2),\ H_2\ (1\ atm) \mid Pt$$

One can see that the two electrolytic solutions are separated by a salt bridge. Now

$$\text{Reaction at the anode: } \frac{1}{2}H_2(1atm) \rightarrow H^+(c_1) + e^- \text{ (oxidation)} \tag{15.50}$$

$$\text{In reduction form: } H^+(c_1) + e^- \rightarrow \frac{1}{2}H_2(1atm) \tag{15.51}$$

$$\text{Reaction at cathode: } H^+(c_2) + e^- \rightarrow \frac{1}{2}H_2(1atm) \tag{15.52}$$

The net cell reaction can be obtained by subtracting equation (15.51) from equation (15.52), e.g.

$$H^+(c_2) \rightarrow H^+(c_1) \tag{15.53}$$

The *e.m.f* of the cell is obtained by writing Nernst equation for the potentials $E_{R(R)}$ and $E_{R(L)}$ of the two electrodes and then subtracting $E_{R(L)}$ from $E_{R(R)}$

$$\begin{aligned} E_{cell} &= E_{R(R)} - E_{R(L)} \\ &= \frac{RT}{F} lnc_2 - \frac{RT}{F} lnc_1 \\ &= \frac{RT}{F} ln \frac{c_2}{c_1} \end{aligned} \tag{15.54}$$

Similar expression of cell *e.m.f.* can be obtained for the zinc concentration cell without transference

$$Zn(s) \mid Zn^{2+}(c_1) \parallel Zn^{2+}(c_2) \mid Zn(s)$$

15.17.3 *Concentration cell formed from two electrochemical cells*

Another type of concentration cell without transference may be set up by combining two electrochemical cells. Let us consider the following cell

$$Pt, H_2\ (1\ atm) \mid HCl(c_1) \mid AgCl(s) \mid Ag(s)$$

In this cell hydrogen electrode and silver-silver chloride electrode are immersed in the same solution of *HCl* of concentration c_1. If another similar cell with *HCl* of concentration c_2 is connected in opposition, the following concentration cell without transference will be formed:

$$Pt \mid H_2\ (1\ atm) \mid HCl(c_1) \mid AgCl(s) \mid Ag(s) - Ag(s) \mid AgCl(s) \mid HCl(c_2) \mid H_2\ (1\ atm) \mid Pt$$

The '– ' sign between the two cells indicates that the cells are placed against each other. It is not difficult to write the overall cell reaction and derive an expression for *e.m.f.* of this type of concentration cell without transference. Let us consider the above cell:

For cell 1 on the left the electrode reactions are:

Anode: $H_2(1\ atm) \rightarrow 2H^+(c_1) + 2e^-$ (oxidation)

In reduction form: $$2H^+(c_1) + 2e^- \rightarrow H_2(1\ atm) \tag{15.55}$$

Cathode: $$2AgCl(s) + 2e^- \rightarrow 2Ag(s) + 2Cl^-(c_1) \tag{15.56}$$

Subtraction of equation (15.55) from (15.56) gives the overall reaction:

$$2AgCl(s) + 2e^- - 2H^+(c_1) - 2e^- \rightarrow 2Ag(s) + 2Cl^-(c_1) - H_2(1 atm)$$

or $$H_2(1 atm) + 2AgCl(s) \rightarrow 2H^+(c_1) + 2Cl^-(c_1) + 2Ag(s) \tag{15.57}$$

For the cell on the right hand side, the reverse reaction will take place except that the concentration of *HCl* is c_2. In other words

$$2H^+(c_2) + 2Cl^-(c_2) + 2Ag(s) \rightarrow H_2(1 atm) + 2AgCl(s) \tag{15.58}$$

Addition of equations (15.57) and (15.58) will give the net cell reaction:

$$HCl(c_2) \rightarrow HCl(c_1)$$

The Nernst equation for this cell is

$$E_{cell} = -\frac{RT}{F} ln \frac{(c_{HCl})_1}{(c_{HCl})_2},$$

since E^o of the two cells cancel each other.

15.18 Application of E.M.F. Measurements

Most applications are based on the fact that the *e.m.f.* of a cell depends on the concentration of the ions with respect to which the electrodes are reversible. Some of the applications are described here:

(a) Measurement of the free energy change of chemical reactions, and the determination of the equilibrium constants from the value of $\Delta G°$. These have been shown in *Sections 15.15.3 and 15.15.4.*

(b) Determination of the solubility product of sparingly soluble salts.

For some cells the overall reaction corresponds to the solution of a sparingly soluble salt. In such cases the measured equilibrium constant is the solubility product of the salt. As an example consider the cell

$$Ag(s) | Ag^+(aq) \| Br^-(\text{aq}) \mid AgBr(s), Ag(s)$$

The reactions at the two electrodes and the electrode potentials are

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \qquad E_L^0 = +0.799$$

$$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq) \qquad E_R^0 = +0.071$$

Overall reaction: $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad E° = -0.728$ V

The solubility product, $K_{sp} = [Ag^+] \times [Br^-]$

By using equation (15.36) $\log K_{sp} = \dfrac{nE^0_{cell}}{0.0591}$ (K_{sp} is an equilibrium constant)

$$= \frac{1 \times (-0.728)}{0.0591}$$

$$0.0591 \log K_{sp} = -0.728$$

Hence $K_{sp} = 4.8 \times 10^{-13}$

(c) Potentiometric Titrations

The end points of titration can, in some cases, be conveniently determined from measurements of the potential of certain electrodes. For example for titration of $AgNO_3$ solution with KCl solution a cell is set up with Ag rod dipped in $AgNO_3$ solution in a beaker, the solution being connected to a standard calomel electrode with a salt bridge as shown in Figure 15.10.

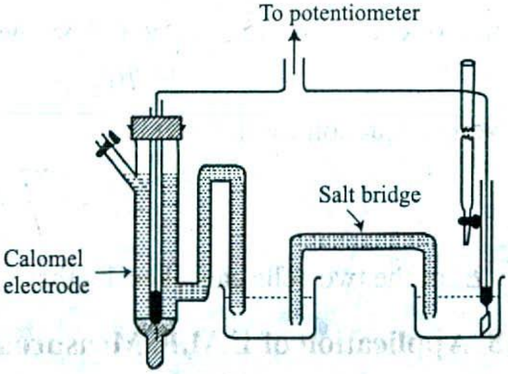


Figure 15.10 Potentiometric titration assembly

KCl solution is added slowly into the *AgNO₃* solution. The *e.m.f.* of the cell is measured after each addition of *KCl* solution. It is observed that the *e.m.f.* changes slowly at first and then drops suddenly, after which the change is again slow. The measured *e.m.f.* when plotted against volume of *KCl* solution added gives a curve as shown in Figure 15.11.The volume which corresponds to the sharp change in potential gives the end point of the precipitation reaction.

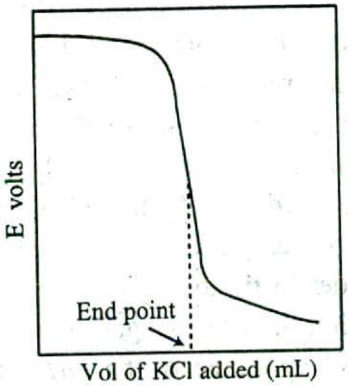


Figure 15.11 Potentiometric titration of $AgNO_3$ with KCl

The end points in oxidation-reduction reactions may likewise be determined from measurement of potential difference between a platinum electrode dipped into the oxidation-reduction system and a calomel electrode. Figure 15.12 shows the results of a titration of ferrous ammonium sulphate solution with standard potassium dichromate solution.

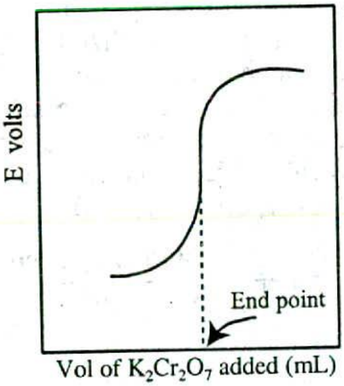


Figure 15.12 Potentiometric titration of Fe^{2+} with $K_2Cr_2O_7$

To facilitate the location of the end point more accurately it is the practice to plot the slope $\Delta E/\Delta V$ of the curve in Figure 15.11 or Figure 15.12 versus the volume V of the titre added as shown in Figure 15.13. The slope $\Delta E/\Delta V$ is usually computed by dividing the differences in potentials in volts by the corresponding differences in volume. The volume V in Figure 15.13 is the mean of the volumes of which the difference is taken.

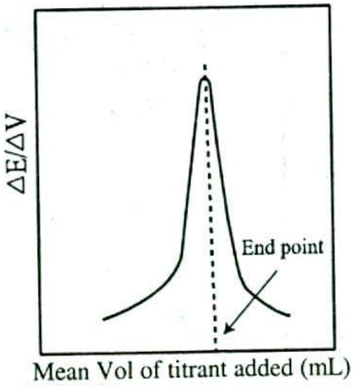


Figure 15.13 Plot of $\Delta E/\Delta V$ *vs* mean volume of titre to ascertain the end point

The end points in acid-base neutralization reactions may also be conveniently determined by potentiometric titrations using a hydrogen electrode or, more conveniently, a glass electrode or a quinhydrone electrode, in combination with a reference electrode like standard calomel electrode. In titrating an acid with a base, at the beginning the *pH* changes slowly, but as the end point is approached the *pH* changes rapidly. Figure 15.14 illustrates the titration curve of a strong acid with a strong base.

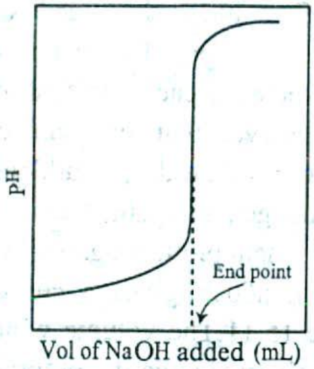


Figure 15.14 *pH*-titration curve of strong acid with strong base

The volume corresponding to the sharp change in *pH* gives the volume of standard alkali required to neutralize the given amount of acid. The sharp change in potential near the equivalence point is due to the large relative change in the concentration of the ion being titrated produced by a small amount of titre added. The equivalence point is the volume of titre required to produce the maximum $\Delta E/\Delta V$. This can be illustrated with the help of Table 15.2, where the calculated values of *pH* during titration of 25 *mL* of 0.10 $mol\ L^{-1}$ HCl, diluted to 100 *mL*, with 0.10 $mol\ L^{-1}$ $NaOH$ is recorded.

Table 15.2 pH change on titrating *HCl* with *NaOH*

mL of *NaOH* added	*pH*	$\Delta pH/\Delta mL$
0.00	1.60	0.02
5.00	1.72	0.03
10.00	1.87	0.04
15.00	2.06	0.06
20.00	2.38	0.14
24.00	3.09	0.82
24.50	3.40	1.30
24.75	3.70	2.20
24.85	3.92	4.80
24.95	4.40	18.00
24.99	5.10	190.00
25.00	7.00	190.00
25.10	9.90	3.00
25.20	1.20	1.30
25.50	10.60	0.60

In performing potentiometric titrations the volume of the titrant is usually kept so large in comparison to the volume of titre added that the volume change during titration may be taken as negligible.

(d) Other important applications of *e.m.f.* measurements are the determination of valencies of ions, transport numbers, study of complex ions etc.

15.19 Lead Storage Cell

Lead storage cell is a kind of Galvanic cell which is extensively used as portable sources of electrical energy in automobiles, diesel generators etc. It is named a storage cell as electricity can be stored by charging the cell over and over again. For use in the above mentioned cases a battery of cells consisting of six or more 2 V cells connected in series are used. Each cell consists of a *Pb* plate as one electrode and a *Pb* plate coated with PbO_2 as another electrode. Both the plates are immersed in a 30% solution of H_2SO_4 of density about 1.84. The cell is

$$Pb(s) \mid H_2SO_4(aq) \mid PbO_2(s), Pb(s)$$

The *Pb*(s) plate and *Pb(s)* plate coated with PbO_2 have different electrode potentials. So, when these are connected a current flows between them. The electrode reactions are:

At left electrode: $Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$

At right electrode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$

The left-side electrode is anode, while the right-side electrode is cathode. The overall cell reaction is

$$Pb(s) + PbO_2(s) + 2H^+(aq) + SO_4^{2-}(aq) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O(l)$$

When the cell is discharging H_2SO_4 is consumed to produce $PbSO_4$ and H_2O. On charging the H_2SO_4 is regenerated. In an automobile the battery is charged by the car generator which acts as a source of *e.m.f.* and reverses the discharge reaction.

15.20 Leclanche's Dry Cell

Leclanche's dry cell is used as flash light battery and in the operation of transistorized equipments. In these cells a carbon rod acting as an inert electrode is surrounded by a paste consisting of manganese dioxide, graphite, a little zinc chloride and an excess of solid ammonium chloride placed in a zinc container. Zinc container acts as the other electrode. The electrode reactions are

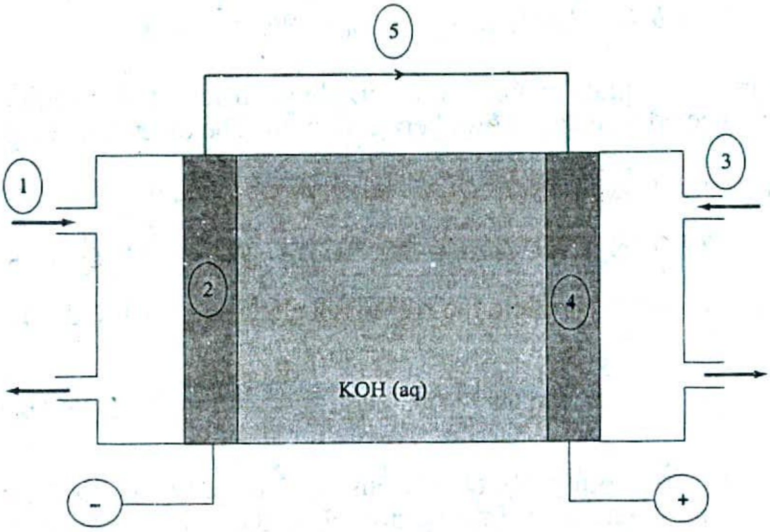
$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$

$$2MnO_2(s) + 2NH_4^+(aq) + 4H_2O(l) + 2e^- \rightleftharpoons 2Mn(OH)_3(s) + 2NH_4OH(aq)$$

As the cell cannot be regenerated after the reactants have been used up it is composed of cheap material. The potential of the cell is about 1·5 V.

15.21 Fuel Cell

At present fossil fuel is the primary source of energy to meet our requirements. But the conversion of fossil fuel either to electrical energy or to thermal energy is an inefficient process, because a significant portion of the energy is lost to the surrounding in the form of heat. Also combustion of fossil fuel generates CO_2 gas which is a greenhouse gas. Efforts are constantly being made to increase the efficiency and reduce the cost of conversion of fossil fuel by electrochemical method in a device known as '*fuel cell*'. The device is also *a form of galvanic cell that requires a continuous supply of reactants to keep it functioning*. The simplest form of fuel cell is a $H_2 - O_2$ fuel cell. In this form of fuel cell hydrogen and oxygen gases are continuously bubbled through an electrolytic solution containing two inert electrodes. Usually KOH solution is used as electrolyte. The anode is made up of porous carbon containing Ni, while the cathode is made up of porous carbon containing Ni and NiO. A schematic diagram is shown in Figure 15.15.



1. stream of H_2, 2. porous cathode, 3. stream of O_2, 4. porous anode
5. Electron flow through external circuit

Figure 15.15 A $H_2 - O_2$ fuel cell

The reactions occurring at the electrodes are as follows:

$$\begin{array}{ll} \text{Anode:} & 2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^- \\ \text{Cathode:} & O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \\ \hline \text{Overall:} & 2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \end{array}$$

The standard *e.m.f.* of this fuel cell has been calculated as +1.23 V. Thus the reaction is spontaneous under standard conditions. American Gemini space probes and Apollo moon probes used the $H_2 - O_2$ fuel cell for the first time. The astronauts used the product of the reaction as drinking water.

Other forms of fuel cells have been devised. Propane-oxygen ($C_3H_8 - O_2$) fuel cell is one of them.

15.22 Polarization and Overvoltage

In discussing the irreversible cell formed by dipping *Zn* and *Cu* rods in H_2SO_4 acid solution it was seen (*Section 15.3*) that when the cell is producing current H_2 gas is evolved at the copper electrode. As the H_2 gas bubbles accumulate on the copper electrode a virtual gas electrode which has an *e.m.f.* opposite to that of the *Cu* electrode is produced. Unless the bubbles are removed the *e.m.f.* of the cell will decrease as a result of the increasing opposing *e.m.f.* at the copper electrode. This change of *e.m.f.* of the cell produced by the products of electrolysis is called *polarization*. Polarization of a cell may occur, (i) due to the change in the concentration of the ions in the neighbourhood of an electrode when the cell is producing current, (ii) when current from an outside source is passed through an electrolytic cell or (iii) when one or more of the steps involved in the electrode reaction are slow. The effect of polarization can be minimized by mechanical or chemical means.

When two clean platinum electrodes are placed in a dilute solution of hydrochloric acid and voltage is applied gradually it is found that when the voltage is low practically no current flows through the circuit, but after a certain voltage is reached the current increases rapidly. The general behaviour is shown by a current density (*i*/area) *vs* potential (*i vs E*) relationship as shown in Figure 15.16.

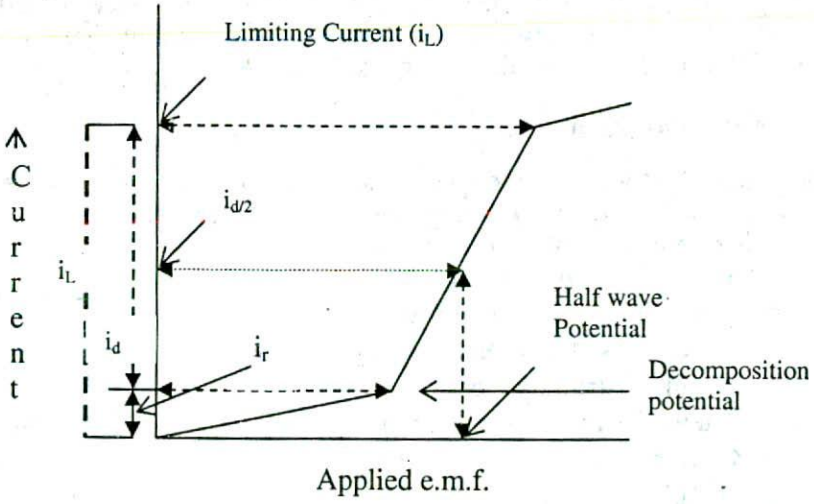


Figure 15.16 Current density plotted against applied voltage

The minimum *e.m.f.* at which the current flows freely corresponds to that at which bubbles of gas are first observed on the electrode. *This minimum e.m.f. that must be applied to bring about continuous electrolysis of the solution of a particular substance is known as the decomposition voltage (also known as discharge potential)* of the electrolyte. As can be seen from Figure 15.16,

(i) the *i vs E* curve starts from zero and with increasing potential a small current flows till the *decomposition potential* is reached.

(ii) the rate of discharge becomes appreciable with slight increase of *e.m.f.*, and the current and the rate of diffusion also increase significantly.

(iii) there is a limit to the rate of diffusion (which also depends on concentration), and as soon as this point is reached further increase of potential does not cause any further increase of current.

The current corresponding to the *limiting rate of diffusion* is called the *limiting current* (i_L). The small current that flows through the cell before the decomposition potential is reached is called *residual current* (i_r). The difference between the limiting current and residual current is called the *diffusion current* (i_d). The potential corresponding to the half of the diffusion current is called *half-wave potential* ($i_d/2$). The half-wave potential is characteristic of a particular ion, and the polarographic method of analysis is based on this principle.

It is found that for most strong acids and bases the decomposition voltage is about 1.7 volts. In a reversible cell containing acids and bases as electrolytes the evolution of gas would theoretically start when the voltage is 1.2. The difference between this potential and the measured decomposition potential is known as the *overvoltage*. The overvoltage depends, besides other factors, on current density and on the nature of the electrode. It may be observed that overvoltage is due to polarization of the electrode.

The overvoltage is important in practical applications of electrochemistry. The high voltage of the lead storage cell is due to the overvoltage of lead. Electro-deposition from acid solution of certain metals, such as zinc, tin or cadmium is possible in spite of their relatively high position in the electromotive series.

15.23 The Polarograph

The potential at which the deposition of metal ions on the cathode starts is known as the *deposition potential* or *discharge potential*. The deposition potentials of different metals are different. A plot of current density versus applied voltage for deposition of metal ions looks like the curve in Figure 15.17. The difference in the deposition potential of metals has been used for analysis by electrolysis in an instrument called *the polarograph,* devised by Heyrovsky and Shikata (1924). It is called the polarograph as it automatically records the plot of current versus voltage. The instrument consists of two electrodes, one of which is made up of mercury falling drop wise from a fine bore capillary glass tube. The other electrode is a pool of mercury at the bottom of the cell. The mercury dropping from the capillary tube presents a fresh surface. In studying reduction phenomena the dropping mercury electrode is made the

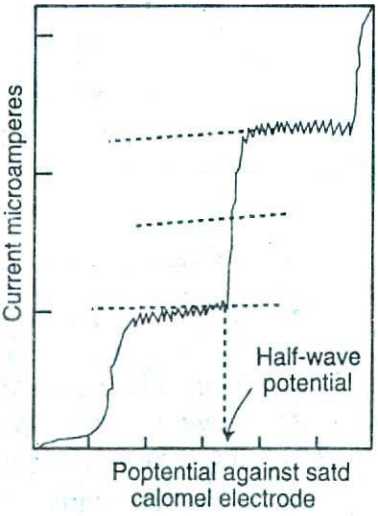


Figure 15.17 A typical polarogram.

cathode and the mercury pool the anode. Sometimes a reference electrode is used as the anode. In an experiment the applied potential is gradually increased and the current flowing through the cell is measured. A schematic polarogram is shown in Figure 15.17. At a certain voltage one of the components on the solution is deposited on the cathode and this is indicated by the sharp rise in the current. The rise is not indefinite, but after a while the current levels off. The levelling off of the current is due to concentration polarization. This current is called the diffusion current as it depends on the rate at which the reducible ions reach the mercury drops. When the voltage reaches the deposition potential of a second component there is again a sharp rise in the current. The rise from one flat portion of the curve to the next is known as the polarographic wave. The potential at the midpoint of the wave, called the *half-wave potential,* is characteristic of the substance being reduced and is independent of the concentration of the reducible species. Observation of the half-wave potentials and comparison with standard tables of half-wave potentials enables one to identify the reducible species in solution. As the diffusion current is dependent on concentration, a quantitative measure of the ion is also possible. An important precaution that has to be taken in polarographic analysis is that oxygen must be carefully eliminated from the solution by bubbling an inert gas through it.

Polarogaphic method of analysis has been highly developed not only for detecting and estimating very small quantities of reducible metal ions but also many organic compounds. The method can also be used for analysis of oxidizable species by reversing the electrodes.

QUESTIONS AND PROBLEMS

1. Discuss the use of galvanic cell as a device for converting chemical energy into electrical energy.
2. What is the relation between the electrical energy that can be produced from a galvanic cell and the potential of the cell? What determines the value of *n* in this expression?
3. What is a standard hydrogen electrode? Describe how it can be set up. Why is it necessary to use such a standard electrode?
4. Describe how the *e.m.f.* of a cell is measured.
5. What is a salt bridge? Why is it used? What determines the suitability of a substance for preparing a salt bridge?
6. What is meant by the standard reduction potential of an electrode? Discuss the importance of the values of standard electrode potentials in physicochemical calculation.
7. Use the standard reduction potentials from the Table to determine whether the following reactions will occur spontaneously:

   (a) $Fe^{3+} + Sn \rightarrow Fe^{2+} + Sn^{2+}$, (b) $Cu + H^{+} \rightarrow Cu^{2+} + H_2$;
   (c) $Mg^{2+} + Al \rightarrow Al^{3+} + Mg$; (d) $Mn + Zn^{2+} \rightarrow Mn^{2+} + Zn$;
   (e) $Cu^{2+} + Cl_2 \rightarrow Cu + Cl^{-}$; (f) $O_2 + Cl^{-} + H^{+} \rightarrow H_2O + Cl_2$
8. Describe the Weston cadmium cell. What chemical reactions account for the operation of the cell?
9. Calculate the *e.m.f.* of the cell at 25°C

$$Zn(s) / Zn^{2+} (\, c = 4 \times 10^{-4}\ mol\ L^{-1}) \,||\, Cd^{2+}(c = 0.20\ mol\ L^{-1}) / Cd(s)$$

   (a) Write the cell reaction; (b) Calculate ΔG for the reaction. [Ans. 0.440 V; (b) –84.9 *kJ mol*$^{-1}$]

10. Describe the construction of: (a) the Weston cadmium cell, (b) the calomel electrode. How would you use them to determine the solubility of silver chloride?

11. Devise an electrochemical cell in which the following reaction takes place.

$$AgBr\,(s) \rightleftharpoons Ag^+\,(aq) + Br^-\,(aq)$$

Calculate the equilibrium constant (solubility product) for this reaction at 25°C. [Ans. 1.0×10^{-12}]

12. Write the half-cell reactions for the following cells and state whether the cell reaction will occur spontaneously as written (Use table of reduction potentials):

$$(a)\ Pt/Fe^{2+},\ Fe^{3+}\ ||\ Zn^{2+}\ |Zn$$

$$(b)\ Cd|\,Cd^{2+}\ ||\ Ag^+|Ag$$

13. Answer the following questions concerning reactions at standard conditions:
   - (a) Can Sn^{2+} reduce Cu^{2+} to Cu?
   - (b) Will Pb liberate H_2 from acids?
   - (c) Can Ag^+ oxidize Zn to Zn^{2+}?
   - (d) What is the *e.m.f.* of the cell in which the following reaction takes place?

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag.$$

14. Calculate the potential of the following cell at 25°C:

$$Pb\,/Pb^{2+}\,(c = 0.02\ mol\ L^{-1})\ ||\ Cl^-\,(c = 0.10\ mol\ L^{-1})\ Cl_2\,/Pt$$

[Ans. 1.595V]

15. Describe the working of the lead storage cell and a flash light battery.

16. Calculate the reduction potential of an electrode consisting of a platinum foil immersed at 25°C in a solution in which the concentrations of ferric and ferrous ions are 0.02 and 0.1 mol L^{-1} respectively.

[Ans. – 0.730 V]

17. Discuss the use of quinhydrone in a hydrogrn electrode. How does a glass electrode function?

18. Write notes on: (a) reversible cells, (b) concentration cells, (c) liquid junction potential, (d) overvoltage, (e) polarograph.

19. Calculate the potential generated by a concentration cell consisting of a pair of iron electrodes dipping in to two solutions, one containing 0.10 $mol\ L^{-1}\ Fe^{2+}$ and the other containing 0.0010 $mol\ L^{-1}\ Fe^{2+}$.

20. Explain how the enthalpy of a reaction can be determined by measurements of the *e.m.f.* of a cell in which the reaction may be made to take place.

21. The e.m.f. of the cell

$$Pb\,/\,PbSO_4\ /\ Na_2SO_4(saturated)\ \ /\,Hg_2SO_4\,,\,/Hg\,/Pt$$

is 0.965 V at 298 K. The temperature co-efficient is $1.74 \times 10^{-4}\ V\ K^{-1}$.

(a) What is the cell reaction? (b) What are the values of ΔG and ΔH?

[Ans. (a) $Pb + Hg_2SO_4 \rightleftharpoons PbSO_4 + Hg$; (b) $-186.2\ kJ\ mol^{-1}$; $-176.2\ kJ\ mol^{-1}$]

22. For those reactions in Q. 7 which occur spontaneously (a) write the cells; (b) calculate standard *e.m.f.* of the cells; (c) calculate ΔG^o and equilibrium constants of the reactions taking place in these cells.

23. Given the cell at 25°C

$$Pt\ /Cl_2\,,Cl^-\,(c = 0.1\ mol\ L^{-1})\ \ ||\ Cl^-\,(c = 0.001\ mol\ L^{-1}),\ Cl_2\ /Pt$$

(a) Write the cell reaction; (b) Which electrode is negative? (c) What is the *e.m.f.* of the cell? (d) Is the reaction spontaneous?

[Ans. (a) Cl^- (c = $0.10\ mol\ L^{-1}$) $\rightarrow Cl^-$ (c = $0.001\ mol\ L^{-1}$); (b) Left ; (c) 0.118 V; (d) Yes.]

24. Calculate the *e.m.f.* of a concentration cell containing 0.0020 $mol\ L^{-1}\ Cr^{3+}$ in one compartment and 0.10 $mol\ L^{-1}\ Cr^{3+}$ in the other compartment with $Cr\,(s)$ electrode dipping into each solution.