PREFACE

In a bid to standardize higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific, generic elective, ability and skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry their acquired credits. I am happy to note that the university has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade "A".

UGC (Open and Distance Learning Programmes and Online Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the six semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

Under-Graduate : Chemistry

Choice Based Credit System (CBCS)

Subject : Honours in Chemistry (HCH)

Course Title: Basic Physical Chemistry

Course Code: GE -CH-11

First Print — June, 2021

Printed in accordance with the regulations of the Distance Education
Bureau of the University Grants Commission.

Netaji Subhas Open University

Under-Graduate Degree Programme

Choice Based Credit System (CBCS)
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Course Title: Basic Physical Chemistry
Course Code: GE -CH-11

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UG : CHEMISTRY
(HCH)

Course : Basic Physical Chemistry
Course Code : GE-CH-11

Unit 1 ❒ Chemical Energetic

Contents

1.0 Objectives

After reading this unit, we will be able to:

- define the commonly used terms in thermodynamics and laws of thermodynamics;
- state important principles of thermochemistry;
- explain standard state and standard enthalpies of formations;
- explain enthalpies of solution and dilution;
- solve numerical problems based on the enthalpy changes;
- define bond enthalpy and bond dissociation enthalpy and resonance energy;
- variation of enthalpy of a reaction with temperature – Kirchhoff's equation;
- state the third law of thermodynamics and calculate the absolute entropies of substances.

1.1 Introduction

When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose, $C_6H_{12}O_6$ by the process of photosynthesis requires the absorption of light energy from the sun. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. In this unit we will review some of the fundamental concepts of energy and heat and the relation between them. We will begin the study of thermodynamics, which treats the energetic aspects of change in general, and will finally apply this specifically to chemical change.

1.2. Brief review of thermodynamics and the Laws of Thermodynamics

In this lesson we would come across some frequently used terms. Let us understand the meaning of these terms first.

1.2.1 System and surrounding

System is the part of the physical universe which is under study, while the rest of the universe is surroundings. The system and surroundings are separated by a boundary. The system can be of three different types – open, closed and isolated system. An open system is a system which can exchange both energy and matter with surroundings. A closed system is a system which can exchange energy but not matter with the surroundings. An isolated system is a system which can exchange neither matter nor energy with the surroundings.

1.2.2 State of a system

We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system

1.2.3 Properties of a system

The measurable properties of a system are called state variables. They may be further divided into two main types – extensive properties and intensive properties. Extensive properties are those whose value depends upon the size or mass of the system. Examples of extensive properties are energy, enthalpy, entropy, heat capacity etc. Intensive properties are those whose value is independent of the size or mass of the system, like temperature, refractive index, density, solubility etc., are the examples of intensive property.

1.2.4 Types of processes

The method of bringing about a change in state is called process. Processes could be of different types. The different types of processes are explained below.

a) **Isothermal process:** When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.

b) **Adiabatic Process**: In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic processes there is always a change in temperature.

c) **Isobaric process**: It is a process in which the pressure of the system remains constant. Heating of water in an open vessel is an example of isobaric process.

d) **Isochoric process:** It is a process in which the volume of the system remains constant.

e) **Reversible and irreversible Process:** A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as irreversible processes.

1.2.5 Work, heat and heat capacity

Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other?

Work is a quantity of energy that flows across the boundary of a system by means of a force during a change in its state and is completely convertible into lifting of a mass in the surroundings. So, work appears in only at the boundary of the system and it appears only during change in the state of the system. The SI unit of work is joule (J).

Heat is a form of energy that is exchanged at the boundary between a system and its surroundings by virtue of a difference in temperature between them and flows from a point of higher to a point of lower temperature and causes a change in the state of the system. Since heat is also a form of energy, so its SI unit is joule (J). Heat is said to be positive when energy is transferred to a system from its surroundings and negative when energy is transferred from system to surroundings.

Heat Capacity (C) is defined as the amount of energy as heat needed to raise the temperature of the system by 1 ^{o}C. So, SI unit of heat capacity is joule per Kelvin ($J\,K^{-1}$). Heat capacity is proportional to the amount of substance. So the molar heat capacity or specific heat capacity is defined as the quantity of the heat required to raise the temperature of one unit mass of the substance. Now, the transfer of heat to system can be done under different condition. If the transfer of heat is done under the conditions of constant volume, the associated heat capacity is called as the heat capacity at constant volume (C_v) and if the transfer of heat is done under the conditions of constant pressure, the associated heat capacity is called as the heat capacity at constant pressure (C_p). The values of C_p and C_v for a given solid or liquid systems are not much different. However for gaseous systems the difference in their values is significant and for an ideal gas it is given by the following expression

$$C_p - C_v = R$$

where R is the gas constant.

1.2.6 The Zeroth law of thermodynamics

The Zeroth law of thermodynamics is states that, if two thermodynamic systems, A and B are in thermal equilibrium with a third thermodynamic system, C then the two thermodynamic system (A and B) are also in thermal equilibrium with each other.

1.2.7 The First law of thermodynamics

You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics. It has been found valid for various situations. We state this law as follows:

Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant.

Mathematically the first law of thermodynamics is stated as:

$$\Delta U = q + w$$

where ΔU = change in internal energy, q = heat absorbed by the system, and w = work done on the system.

1.2.8 Internal energy (U)

Every system has a definite amount of energy. This amount is different for different substances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei. The internal energy may be defined as the sum of the energies of all the atoms, molecules or ions contained in the system. It is a state variable. It is not possible to measure the absolute values of internal energy. However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is U_1 and that in the final state is U_2, then change in internal energy ΔU is independent of the path taken from the initial to the final state. We can write this change as:

$$\Delta U = U_2 - U_1$$

The internal energy of the system can be changed in two ways:

(i) either by allowing heat to flow into the system or out of the system; and

(ii) by work done on the system or by the system.

1.2.9 Enthalpy (H)

For measuring heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by

$$H = U + pV$$

Where, U is the internal energy, p is the pressure and V is the volume of the system.

Enthalpy change, ΔH, is given by

$$\Delta H = \Delta U + p\,\Delta V \text{ (at constant pressure)} = q \text{ (at constant pressure)}$$

We denote q at constant pressure by q_p hence

$$\Delta H = q_p$$

So, by measuring heat lost or gained at constant pressure by the system, we can measure enthalpy change for any process.

1.3. Important Principles and Definitions of Thermochemistry

1.3.1 Energy changes accompanying chemical reactions

Majority of chemical reaction are performed under the conditions of constant pressure, so the measured heat changes refer to the enthalpy change for the reaction. Such an enthalpy change associated with a given chemical reaction is termed as the enthalpy of reaction ($\Delta_r H$). Let as denote total enthalpy of reactants as $H_{\text{reactants}}$ and total enthalpy of products as H_{products}. The difference between these enthalpies, $\Delta_r H$, is the enthalpy of the reaction

$\Delta_r H = H_{\text{products}} - H_{\text{reactants}}$

When H_{products} is greater than $H_{\text{reactants}}$ then $\Delta_r H$ is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,

$H_2(g) + I_2(g) \rightarrow 2HI\ (g);\ \Delta_r H = 52.5\ \text{kJ}$

When H_{products} is less than $H_{\text{reactants}}$ then $\Delta_r H$ is negative and heat is evolved in the reaction, and the reaction will be exothermic. For example,

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\ (l);\quad \Delta_r H = -\ 890.4\ \text{kJ}$

Enthalpy of a reaction changes with pressure and temperature.

1.3.2 Thermochemical equations

You are familiar with equations for chemical reactions as the symbolic representation of a given reaction that consists of chemical formulae of the reactant(s) and product(s) and the reaction condition. If we write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below:

(i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) alongside the chemical formulae respectively. For example, to represent burning of methane in oxygen, we write

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l) + \text{heat}$

(ii) In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol $\Delta_r H$. The amount of heat evolved or absorbed is written after the equation followed by semicolon. $\Delta_r H$ is negative for exothermic reactions and it is positive for endothermic reactions. For example:

An exothermic reaction is written as

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)\ ;\ \Delta_r H = -\ 891\ \text{kJ}$

Whereas an endothermic reaction is written as

$H_2\ (g) + I_2\ (g) \rightarrow 2HI\ (g)\ ;\ \Delta_r H = 52.2\ \text{kJ}$

(iii) Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction and the $\Delta_r H$ values given correspond to these quantities of substances.

(iv) In case, if the coefficients are multiplied or divided by a factor, $\Delta_r H$ value must also be multiplied or divided by the same factor. In such cases, the $\Delta_r H$ value will depend upon the coefficients. For example, in equation

$H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O\ (g)\ ;\ \Delta_r H = -\ 242\ \text{kJ}$

If coefficients are multiplied by 2, we would write the equation

$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (g)\ ;\ \Delta_r H = 2\ (-\ 242) = -\ 484\ \text{kJ}$

(v) When a chemical equation is reversed, the value of $\Delta_r H$ is reversed in sign. This is known as Lavoisier – Laplace law. For example

$N_2(g) + 3H_2\ (g) \rightarrow 2NH_3\ (g);\ \Delta_r H = -\ 91.8\ \text{kJ}$

$2NH_3(g) \rightarrow N_2(g) + 3H_2\ (g);\ \Delta_r H = +\ 91.8\ \text{kJ}$

1.3.3 Standard enthalpy of reactions

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. It is denoted by $\Delta_r H^0$. The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

1.3.4 Hess's law of constant heat summation

Hess's law can be stated as follows:

The standard enthalpy change for a reaction is the sum of standard enthalpies of a sequence of reactions (at the same temperature and pressure); the overall reaction should be capable of being represented by the given sequence of reactions.

Hess's law is a direct consequence of the law of conservation of energy i.e. first law of thermodynamics. It is not necessary that every reaction in the given sequence should be conducted in a laboratory. A particular reaction can also be imaginary. The only requirement is that the individual chemical reactions in the sequence must balance and add up to the equation for a particular reaction. Also Hess's law enables arithmetic operations of chemical equations. This law is helpful in calculating enthalpies of reactions which cannot be experimentally determined; what is required is to select a correct sequence of reactions. We give below the use of Hess's law in calculating the enthalpy of conversion of graphite to diamond which is very difficult to determine.

C (graphite) + O_2 (g) → CO_2 (g); $\Delta_r H_1 = -\ 393.5$ kJ

C (diamond) + O_2 (g) → CO_2 (g); $\Delta_r H_2 = -395.4$ kJ

Then subtracting, we get

C (graphite) – C (diamond) = $\Delta_r H_3 = \Delta_r H_1 - \Delta_r H_2 = -393.5$ kJ – (–395.4 kJ) = 1.9 kJ

Hence, we can write

C (graphite) → C(Diamond) $\Delta_r H_3 = 1.9$ kJ

1.4. Standard enthalpies of formations

The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by $\Delta_f H^0$.

When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by $\Delta_f H^0$. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero. For example:

C(Graphite) + O_2(g) → CO_2 (g) ; $\Delta_f H^0 = -\ 393.5$ kJ

This means that carbon dioxide is formed from its elements in their most stable states, carbon in the form of graphite at room temperature and gaseous O_2 and CO_2 being at 1 bar.

1.5. Enthalpies of solution and dilution

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These ions are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)

$$\begin{tikzcd}
\mathbf{AB\ (s)} \arrow[r, "\Delta_{sol}H^0"] \arrow[d, "\Delta_{lattice}H^0"] & \mathbf{A^+(aq) + B^-(aq)} \\
\mathbf{A^+(g) + B^-(g)} \arrow[ur, "\Delta_{hyd}H^0"'] &
\end{tikzcd}$$

The enthalpy of solution of AB(s), $\Delta_{sol}H^0$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice}H^0$ and enthalpy of hydration of ions, $\Delta_{hyd}H^0$ as

$$\Delta_{sol}H^0 = \Delta_{lattice}H^0 + \Delta_{hyd}H^0$$

For most of the ionic compounds, $\Delta_{sol}H^0$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all.

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. For water

$$\text{HCl (g)} + 10\ \text{aq.} \rightarrow \text{HCl.10 aq.}\ \Delta H = -69.01\ \text{kJ / mol}$$

Let us consider the following set of enthalpy changes:

(S-1) $\text{HCl (g)} + 25\ \text{aq.} \rightarrow \text{HCl.25 aq.}\ \Delta H = -72.03\ \text{kJ / mol}$

(S-2) $\text{HCl (g)} + 40\ \text{aq.} \rightarrow \text{HCl.40 aq.}\ \Delta H = -72.79\ \text{kJ / mol}$

(S-3) $\text{HCl (g)} + \infty\ \text{aq.} \rightarrow \text{HCl.}\ \infty\ \text{aq.}\ \Delta H = -74.85\ \text{kJ / mol}$

The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain–

$HCl.25\ aq. + 15\ aq. \rightarrow HCl.40\ aq.\ \Delta H = [\,-72.79 - (-72.03)]\ kJ / mol$

$= -\,0.76\ kJ / mol$

This value (–0.76 kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

1.6. Bond energy, bond dissociation energy and resonance energy

In a chemical reaction, we have seen that energy is either absorbed or evolved. The origin of this energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only. At high temperature, hydrogen molecules dissociate into atoms as

$H_2\,(g) \rightarrow H\,(g) + H\,(g);\ \Delta_r H^0 = 435\ kJ/mol$

The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the H_2 molecules. For a diatomic molecule like $H_2(g)$, we define bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms.

Now, let us consider a polyatomic molecule like CH_4 (g). The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in

$CH_4\,(g) \rightarrow CH_3\,(g) + H\,(g);\ \Delta_r H^0 = 431.8\ kJ/mol$

$CH_3\,(g) \rightarrow CH_2\,(g) + H\,(g);\ \Delta_r H^0 = 471.1\ kJ/mol$

$CH_2\,(g) \rightarrow CH\,(g) + H\,(g);\ \Delta_r H^0 = 421.7\ kJ/mol$

$CH\,(g) \rightarrow C\,(g) + H\,(g);\ \Delta_r H^0 = 338.8\ kJ/mol$

We can observe here that each of these equation represent the dissociation of C-H bond but the energies required for them are different. Though all the C-H bond in CH_4 are equivalent, the dissociation energies are not same. This is due to the fact that once a C-H bond dissociated, the remaining species has different electronic distributions.

We can add these four equations to get

CH_4 (g) → C (g) + 4H (g); $\Delta_r H^0 = 1663.4$ kJ/mol

In this reaction the methane molecule has got converted into its constituent atoms therefore the enthalpy change is called enthalpy of atomization of methane. If we divide the enthalpy of atomization of methane by 4, we get an average value (1663.4/4 = 415.9 kJ/mol) for the bond enthalpy for C-H bond.

Now if we want to determine the bond enthalpy in ethane (C_2H_6), here two types of bond exist, C-H and C-C. We assume that the bond enthalpy for C-H bond in ethane is same as that of methane. The atomization of ethane is given by the expression

C_2H_6 (g) → 2C (g) + 6H (g); $\Delta_r H^0 = 2842.4$ kJ/mol

The enthalpy of atomization of ethane would be equal to the bond enthalpies of six C-H bond and one C-C bond. If we subtract the bond enthalpies of six C-H bonds from the enthalpy of atomization we can get the bond enthalpy for C-C bond. Thus, bond enthalpy for a given bond refers to the average bond dissociation energy for the same bond in a number of molecules having the said bond. Using Hess's law, bond enthalpies can be calculated. Again bond enthalpy data can be used to calculate $\Delta_r H$ for a chemical reaction occurring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products.

$\Delta_r H = \Sigma$ B.E. (reactants) – Σ B.E. (products).

Using bond energy and enthalpy of formation data resonance energy in a molecule can be calculated. When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Resonance energy = Experimental or actual heat of formation - Calculated heat of formation.

For example the resonance energy of N_2O can be calculated if observed $\Delta_f H^o$ (N_2O) is 82 kJ mol^{-1}, B.E of N ad N is 946 kJ mol^{-1}, B.E of N ≡ N is 418 kJ mol^{-1}, B.E of O = O is 498 kJ mol^{-1}; B.E of N = 0 is 607 kJ mol^{-1}.

So we can write, $N_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O$

In another way we can write, $N \equiv N + \frac{1}{2}O = O \rightarrow N = N = O$

So, calculated $\Delta_f H^o$ (N_2O) = [B.E $_{(Na=N)}$ + B.E $_{(O = O)}$] – [B.E $_{(N=N)}$ + B.E $_{(N=O)}$]

$$= \left[946 + \frac{498}{2}\right] - [418 + 607] = +\ 170 \text{ kJ/mole}$$

Hence, Resonance energy = observed $\Delta_f H^o$ – calculated $\Delta_f H^o$

$$= 82 - 170 = -\ 88 \text{ kJ/mol}$$

1.7. Variation of enthalpy of a reaction with temperature – Kirchhoff's equation

We have learnt that the enthalpy of different types of reactions can be calculated with the help of enthalpy of formation of different compounds. However, most of the data available on enthalpy of reaction or enthalpy of formation of compounds are at 298 K. If the enthalpy of reaction required at some other temperature, we need to know the temperature dependence of the enthalpy of reaction. The enthalpy of reaction at a desired temperature can be obtained from the enthalpy of reaction at some other temperature with the help of Kirchhoff's equation. Let us derive Kirchhoff's equation.

We know that: $\Delta_r H^0 = H^0(\text{products}) - H^0(\text{reactants})$

Differentiating with respect to temperature we get,

$$\frac{d}{dT}\left(\Delta_r H^0\right) = \frac{d}{dT}H^0(\text{products}) - \frac{d}{dT}H^0(\text{reactants})$$

As $\frac{d}{dT}H^0 = C_p^0$ we can write

$$\frac{d}{dT}\left(\Delta_r H^0\right) = C_p^0(\text{products}) - C_p^0(\text{reactants})$$

$$\frac{d}{dT}\left(\Delta_r H^0\right) = \Delta C_p^0$$

Writing the equation in differential form

$$d\left(\Delta_r H^0\right) = \Delta C_p^0 dT$$

Integrating the equation between temperature T_1 and T_2,

$$\int_{T_1}^{T_2} d\left(\Delta_r H^0\right) = \int_{T_1}^{T_2} \Delta C_p^0 dT$$

$$\Delta_r H^0(T_2) - \Delta_r H^0(T_1) = \Delta C_p^0 \left(T_2 - T_1\right)$$

Rearranging,

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \Delta C_p^0 \left(T_2 - T_1\right)$$

This is the Kirchhoff's equation that gives the temperature dependence of enthalpy change for a reaction.

1.8. Third Law of thermodynamics and calculation absolute entropies of substances

The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing q_{rev}/T increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

1.9. Summary

In this unit we have started our discussion by revisiting the important terms and laws of thermodynamics. Then we have focused our discussion on thermochemistry – the study of the heat changes associated with chemical reactions. We have discussed about important principles and definitions of thermochemistry. We have highlighted the concept of standard state and standard enthalpies of formations, enthalpies of solution and dilution. We have shown how to calculate bond energy, bond dissociation energy and resonance energy from thermochemical data. Variation of enthalpy of a reaction with temperature is discussed and Kirchhoff's equation was derived. Finally third law of thermodynamics was stated and calculation absolute entropies of substances were discussed.

1.10. Questions

1. What is standard enthalpy of a reaction?
2. Why the formation enthalpy of Graphite is taken as zero?
3. What is an exothermic and endothermic reaction?
4. Describe Hess's law and explain.
5. Derive the Kirchhoff's equation relating to the effect of temperature on the reaction enthalpy of a reaction.
6. Calculate $\Delta_r H^o$ for the reaction C (graphite) + O_2 (g) → CO (g) at 298 K., using the following thermochemical equations:

   C (graphite) + O_2 (g) → CO_2 (g); $\Delta_r H^o = -393.5$ kJ

   CO (g) + 1/2O_2 (g) → CO_2 (g); $\Delta_r H^o = -283.5$ kJ

   (Ans. -110 kJ)

Unit 2 ❐ Chemical Equilibrium

Contents

2.0. Objectives

After going through this unit, we will be able to know about

- reversible and irreversible reactions.
- free energy change in a chemical reaction.
- law of mass action.
- relation between free energy and equilibrium constant
- express the equilibrium constant in different ways
- Le Chatelier's principle and its applications.

2.1. Introduction

In general, chemical reactions can be divided into two types - reversible and irreversible.

Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. So in the irreversible reactions, the same reactants cannot be formed back from the products under normal set of experimental conditions. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available are reversible reactions. This stage of the system is the dynamic equilibrium and the rates of the forward and reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. The present unit discusses the meaning of this state of equilibrium and how the equilibrium composition of the reactants and products are correlated with change in Gibb's free energy.

2.2. Free energy change in a chemical reaction

While discussing about the criteria for reversible and irreversible reactions in thermodynamics, it was concluded that if the free energy change of a chemical reaction is negative, the reaction can take place spontaneously, that is it is feasible. If the free energy change is zero, the reaction is in a state of equilibrium and if the free energy change is positive, the reaction would not proceed. By definition, $G = H - TS$ so that, at constant temperature,

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

where, ΔG is the change in free energy of the reaction, ΔH is the change in enthalpy of the reaction and ΔS is the change in entropy of the reaction.

From the above equation it is evident that the spontaneity of the reaction is dependent on the overall value of the two factors - energy factor ÄH and the entropy factor, $T\Delta S$. For a reaction to be spontaneous, ΔG value should be negative. For this, ΔH should be negative and $T\Delta S$ should be positive. When both factors are favourable then the value of ΔG will have large negative value, and the reaction will be highly feasible.

Now suppose the energy factor is favourable, i.e., ΔH is negative, but the entropy factor is not favourable i.e., $T\Delta S$ is also negative. In such case, the feasibility of the reaction will be determined by the factor which predominates. So if the numerical value of ΔH is greater than $T\Delta S$, then the reaction is feasible.

Again, if the energy factor does not favour, i.e., ΔH has a positive value but the entropy factor favours the reaction, i.e., $T\Delta S$ is positive then the reaction will occur if $T\Delta S$ is numerically greater than ΔH.

If neither energy factor nor entropy factor predominates then ΔH is numerically equal to TΔS. Then the value of ΔG will be zero. Under these circumstances, the reaction will be in a state of equilibrium, i.e., no net reaction will occur in any direction.

Standard free energy change (ΔG^o): The standard free energy change of a reaction is defined as the free energy change of a reaction when the reactants and products are in their standard states (25 °C, 1 atm pressure). At this condition the equation 1 may be written as

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (2)$$

where ΔH^o is the standard enthalpy change of the reaction and ΔS^o is the standard entropy change of the reaction at the temperature T.

2.3. Law of mass action

Our experimental observations tell us that most of the chemical reactions when carried out in closed vessels do not go to completion. The reactants may still be present but they do not appear to change into products. In this situation the rate of the back reaction becomes equal to the rate of the forward reaction. The composition of the reaction mixture at a given temperature is the same irrespective of the initial state of the system, i.e., irrespective of the fact whether we start with the reactants or the products. The reaction is said to be in a state of equilibrium. The attainment of equilibrium can be recognised by noting constancy of observable properties such as pressure, concentration, density or whichever may be suitable in a given case. The relationship between the quantities of the reacting substances and the products formed can be correlated readily with the help of the law of mass action.

The law of mass action may be stated as follows:

The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is directly proportional to the product of the active masses of the reacting substances.

If we consider a general chemical reaction

$$aA + bB \rightleftharpoons mM + nN$$

According to the law of mass action, assuming that active masses are equivalent to the molar concentration,

the rate of the forward reaction, $r_f \propto [A]^a[B]^b$ i.e. $r_f = k_f[A]^a[B]^b$

and the rate of the reverse reaction, $r_r \propto [M]^m [N]^n$ i.e, $r_r = k_r[M]^m[N]^n$

where k_f and k_r are proportionality constants and square brackets represent the molar concentration of the entities enclosed. The constant $k\text{-}_f$ is rate constant of the forward reaction and k_r is the rate constant of the reverse or backward reaction. Now at equilibrium, the rate of forward reaction is equal to the rate of the reverse reaction, that is,

$$k_f[A]^a[B]^b = k_r[M]^m[N]^n$$

$$\therefore \frac{k_f}{k_r} = K_{eq} = \frac{[M]^m[N]^n}{[A]^a[B]^b} \qquad (3)$$

The constant K_{eq} is called the equilibrium constant of the reaction. Equilibrium constant being the ratio of the concentrations raise to the stoichiometric coefficients. Therefore, the unit of the equilibrium constant = $\left[\text{Mole L}^{-1}\right]^{\Delta^n}$.

where, Δn = (sum of stoichiometric coefficients of products – sum of stoichiometric coefficients of reactants)

Equation 3 represents the law of chemical equilibrium.

The equilibrium concentrations in equation 3 can be written in terms of activities (a_i), partial pressure (p_i), molar concentrations (c_i) or mole fraction (x_i) of the species involved in the reaction. Consequently, K_{eq} will have different numerical values for a given chemical reaction.

Example 1: Calculate Kc for the reaction, H_2 (g) + $I_2 \leftrightarrow$ 2HI (g), if the reaction had been started with 1 mole of H_2 (s) and 3 mole of I_2 (g). At the equilibrium the moles of HI formed is 1.5 moles. The volume of the reaction vessel is 2 litre.

Solution:

	$H_2(g)$ +	$I_2 \leftrightarrow$	$2HI(g)$
Initially moles	2	3	0
Moles at eqm.	2 – x	3 – x	2x
Conc. of eqm.			

From question, 2x = 1.5

x = 0.75

$[H_2] = (2–x)/2 = 1.25/2$

$[I_2] = (3–x)/2 = 2.25/2$

$[HI] = 1.5/2$

Therefore K_c for the reaction = $[HI]^2 / [H_2].[I_2]$

By putting the values we get Kc = 0.8

2.4. Thermodynamic Derivation of the Law of Chemical Equilibrium

Consider once again the general reversible chemical reaction

$$aA + bB \rightleftharpoons mM + nN$$

where the reactants and the products are assumed to be ideal gases.

We know that chemical potential (i.e., Gibbs free energy) of reactants consisting of *a* moles of A and *b* moles of B is given by the expression

$$G_{\text{reactants}} = a\mu_A + b\mu_B \tag{4}$$

where μ_A and μ_B are the chemical potentials of the species A and B, respectively. Similarly, for the products we have

$$G_{\text{products}} = m\mu_M + n\mu_N \tag{5}$$

In each case, pressure and temperature are constant. The free energy of the reaction is equal to the difference between the free energy of the products and that of the reactants. So

$$\begin{aligned}(\Delta G)_{\text{reaction}} &= G_{\text{reactants}} - G_{\text{products}}\\ &= (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \qquad (6)\end{aligned}$$

Now at equilibrium, the free energy change $\Delta G = 0$. So the equation 6 becomes

$$(m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0 \tag{7}$$

The chemical potential of the *i*th species in the gaseous state is given by

$$\mu_i = \mu_i^0 + RT \ln p_i \tag{8}$$

where, p_i is the partial pressure of the *i*th component and the μ_i^0 is its standard chemical potential (i.e., when the partial pressure of the *i*th component is unity). So from equation 7 and 8 we can obtain

$$\left[m\left(\mu_M^0 + RT\ln p_M\right) + n\left(\mu_N^0 + RT\ln p_N\right)\right] -$$

$$\left[a\left(\mu_A^0 + RT\ln p_A\right) + b\left(\mu_B^0 + RT\ln p_B\right)\right] = 0 \qquad (9)$$

or $$RT\ln\frac{p_M^m\, p_N^n}{p_A^a p_B^b} = -\left[\left(m\mu_M^0 + n\mu_N^0\right) - \left(a\mu_A^0 + b\mu_B^0\right)\right]$$

$$= -\left[G^0_{\text{products}} - G^0_{\text{reactant}}\right]$$

$$= -\left(\Delta G^0\right)_{\text{reaction}} \qquad (10)$$

or, $$\frac{p_M^m\, p_N^n}{p_A^a p_B^b} = e^{-\Delta G^0/RT} \qquad (11)$$

Since ΔG^0 depends only on temperature and R is the gas constant, hence the right hand side of equation 11 is a constant at constant temperature. Thus

$$\frac{p_M^m\, p_N^n}{p_A^a p_B^b} = \text{constant} = K_p \qquad (12)$$

This is the law of chemical equilibrium.

It can be easily shown that if the chemical potentials of the various species are expressed in terms of mole fractions (x_i), then

$$\mu_i = \mu_i^0 + RT\ln x_i \qquad (13)$$

So we obtain similar equation like equation 12

$$\frac{x_M^m\, x_N^n}{x_A^a x_B^b} = K_x \qquad (14)$$

If the chemical potentials of the various species are expressed in terms of molar concentrations (c_i), then

$$\mu_i = \mu_i^0 + RT \ln c_i \tag{15}$$

From which we obtain the following expression

$$\frac{c_M^m \, c_N^n}{c_A^a c_B^b} = K_c \tag{16}$$

Equation 12, 14 and 16 are the expressions of Kp, Kx, and Kc respectively.

van't Hoff reaction isotherm:

From equation 11 and 12 we can have

$$K_{eq} = e^{-\Delta G^0 / RT} \tag{17}$$

or $$\Delta G^0 = -RT \ln K_{eq} \tag{18}$$

The equation 18 is called van't Hoff reaction isotherm. It may be used to calculate the change in free energy of a reaction in the standard condition (ÄG^0) from the equilibrium constant and vice-versa.

2.5. Distinction between ΔG and ΔG^0

For a reaction ΔG^0 is the difference in the free energy of products and reactants when all of them are in their standard states. This does not refer to the actual reaction at equilibrium. ΔG, however, refers to the difference in the free energy of products and reactants at the actual measured concentrations (or partial pressures) of the components. When $\Delta G=0$, the reaction is at equilibrium and the concentrations (or the partial pressures) of the components are those which appear in the equilibrium constant expression.

2.6. Relationships between K_p, K_c and K_x for reactions involving ideal gases

Relation between K_p and K_c:

For an ideal gaseous mixture we can write

$$p_iV = n_iRT$$

$$p_i = \frac{n_i}{V}RT = c_iRT$$

Where, c_i ($=n_i/V$) is the molar concentration of the *i*th component in the mixture of total volume V.

For the reaction

$$aA + bB \rightleftharpoons mM + nN$$

We can write, $p_A = c_ART$, $p_B = c_BRT$, $p_M = c_MRT$, $p_N = c_NRT$

So from equation 12 we get

$$K_p = \frac{p_M^m p_N^n}{p_A^a p_B^b} = \frac{(c_MRT)^m (c_NRT)^n}{(c_ART)^a (c_BRT)^b} = \frac{c_M^m c_N^n}{c_A^a c_B^b}(RT)^{(m+n)-(a+b)}$$

$$= K_cRT^{\Delta n}$$

where $\Delta n = (m + n) - (a + b)$

Relation between K_p and K_x:

In an ideal gaseous mixture, each component obeys Dalton's law of partial pressure, i.e.,

$$p_i = x_iP$$

where, P is the total pressure and p_i is the partial pressure of the *i*th component with mole fraction x_i in the mixture.

For the reaction

$$aA + bB \rightleftharpoons mM + nN$$

we have $p_A = x_AP$, $p_B = x_BP$, $p_M = x_MP$, $p_N = x_NP$

$$K_p = \frac{p_M^m p_N^n}{p_A^a p_B^b} = \frac{(x_MP)^m (c_NP)^n}{(x_AP)^a (c_BP)^b} = \frac{x_M^m x_N^n}{x_A^a x_B^b}(P)^{(m+n)-(a+b)} = K_xP^{\Delta n} \qquad (20)$$

where $\Delta n = (m + n) - (a + b)$

So from equation 19 and 20 we can write

$$K_p = K_c RT^{\Delta n} = K_x P^{\Delta n} \tag{21}$$

This is the relation between different equilibrium constants.

If $\Delta n = 0$, $(m + n) = (a + b)$ (i.e., the number of moles of products equals to the number of moles of reactants), then

$K_p = K_c = K_x$

2.7. Le Chatelier's principal

The equilibrium expressions derived so far are very useful to perform numerical computations to check the effects of change in pressure, temperature or volume for a system under equilibrium. We can find out the effect of such factors on the system under equilibrium with the help of expressions such as, Eq. 12, 14 and 16. However, often one is more interested in predicting qualitatively the results of a change brought about by external forces on the system under equilibrium. The effect of concentration, temperature and pressure on a system in equilibrium can be predicted with the help of a generalization first proposed by a French chemist Le-Chetelier in 1884. After his name, this generalization is known as Le-Chatelier's principle. It states as follows:

If a stress is applied to any system under equilibrium, the system would tend to shift in such a way so as to neutralise the effect of that stress (if possible).

The stress for a chemical reaction could be in the form of a change in pressure, temperature or concentration at equilibrium. According to the above principle then, the equilibrium would shift in such a direction so that the effect of these, changes is neutralised. We shall consider the effect of each one of these factors on equilibrium.

2.7.1 Effect of change of concentration

Let us consider the following reaction at equilibrium,

$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

Now, if we add some H_2 to the equilibrium mixture, it will disturb the equilibrium. According to Le Chatelier's principle, the equilibrium would shift in such a way so as to oppose the effect of this excess H_2. It can do so by using up this excess H_2 to react with more I_2 to give more of HI. We describe this process by saying that the final position of equilibrium has shifted to the right of the equation. In this final state of equilibrium, then, more amount of HI is formed as compared to earlier equilibrium state. Just the opposite would be the fate of the reaction if, instead of H_2 some HI is added to the system under equilibrium. In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction so that the value of the equilibrium constant remains the same.

2.7.2 Effect of change of pressure

If we consider the above reaction again and suppose that the pressure of the system is increased by reducing the volume of the container, the system should react in such a way so as to reduce the effect of the increase in pressure. However there is no way - by which this can be achieved. The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products.

However, the situation changes if we consider the synthesis of ammonia:

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

If the pressure of the system is increased at the equilibrium as was done in the previous example, the effect of this increase could be eliminated by the formation of more ammonia. This becomes obvious if you realise that the total number of moles of the reactants is four as compared to the moles of product which is two. Four moles will exert greater pressure than two moles, so, if the system wants to reduce the extra pressure, it can do so by moving in the forward direction. On the other hand, if we decrease the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen. Thus, if we want to produce ammonia in the industry, it is preferable to carry out the reaction at high pressures.

Comparing the two reactions given above, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total numbers of moles of the reactants are different from the total number of moles of the products.

2.7.3 Effect of change of temperature

Consider once again the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction.

N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) $\Delta H = -92.38$ kJ

If the temperature of the system is increased at equilibrium then according to Le Chatelier's principle, the system should react in such a way so as to neutralise this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and, therefore, the reverse reaction of decomposition of ammonia will be endothermic. Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards left. This will increase the amounts of N_2 and H_2 and decrease the amount of NH_3 at equilibrium.

We can generalise this observation as with the increase of the temperature of the system the amount of the products will decrease and the amount of the reactants will increase for an exothermic reaction. Just the opposite will be true for all endothermic reactions. The effect of these factors gains special importance for the production of a substance on large scale. In any industrial production of a substance it is imperative to know the optimum conditions of temperature, pressure and concentrations in order to get the maximum yield at a minimum cost. For instance, in the production of ammonia we know from Le Chatelier's principle that high pressure and high concentration of N_2 and H_2 will favour the reaction. Similarly, the above principle also predicts that the reaction would be more favourable at low temperatures since it is exothermic. However, we cannot carry out the reaction at a very low temperature because the rate of the reaction becomes too slow at lower temperatures. Hence the reaction is performed at pressures of several megapascals and at a optimum temperatures between 650 and 750 K in presence of finely divided iron as catalyst.

2.7.4 Effect of catalyst

There is no effect on addition of a catalyst on the equilibrium state. This is because catalyst increases the rate of forward reaction as well as rate of backward reaction to the same extent. It simply helps to achieve the equilibrium quickly. It may be further noted that catalyst has no effect on the equilibrium concentration of a reaction mixture.

2.8. Summary

In this unit we have discussed reversible and irreversible reaction and the free energy change in a chemical reaction. Then we have discussed the meaning of chemical equilibrium and the law of mass action. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression were then utilised in understanding the equilibrium. We then learnt Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by the changes brought about in concentration, temperature and pressure in the system.

2.9. Questions

1. Describe the Law of mass action.
2. Derive the relation between K_p and K_c.
3. Write a short note on Le Chatelier's principal.
4. Explain the effect of pressure and temperature in the following reaction

   $N_2 (g) + O_2 (g) \rightleftharpoons 2NO\ (g); \Delta H = -43.2$ kJ
5. At 20 °C the K_p of the reaction $2NO (g) + Cl_2 (g) \rightleftharpoons 2NOCl (g)$ is 1.9×10^{-3} atm^{-1}. Calculate the value of K-$_c$ at that temperature.

   (Ans. 45649.4 L mol^{-1})
6. At equilibrium, the concentrations of $N_2 = 3.0 \times 10^{-3}$ M, $O_2 = 4.2 \times 10^{-3}$ M and $NO = 2.8 \times 10^{-3}$ M in a sealed vessel at 800 K. What will be K_c for the reaction

   $N_2 (g) + O_2 (g) \rightleftharpoons 2NO\ (g)$ (Ans. 0.622)

Unit 3 ❐ Ionic Equilibrium

Contents

3.0. Objectives

After going through this unit, we will be able to know about

- Strong and weak electrolytes.
- Degree of ionization.
- Ionic product of water.
- pH scale and pH calculation.
- Common ion effect and its applications.
- Salt hydrolysis.
- Buffer solution and buffer action.

- Solubility and solubility product of sparingly soluble salts.
- Application of solubility product in precipitation reaction.

3.1. Introduction

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

3.2. Strong and weak electrolytes

An electrolyte is defined as a compound whose aqueous solution or molten state conducts electricity. On the other hand, a compound whose aqueous solution or molten state does not conduct electricity is called a non electrolyte. The conductance by an electrolyte is due to the presence of ions produced by the dissociation of the substance. However, different electrolytes dissociate to different extents. Acids, bases and salts come under the category of electrolytes.

Depending upon the degree of dissociation or ionization, the electrolytes are divided into two categories, called ‘strong electrolytes’ and ‘weak electrolytes’.

Strong Electrolytes: These are the substances which dissociate almost completely into ions in aqueous solution and hence are a very good conductor of electricity.

Examples:

Acid: HCl, HNO_3, H_2SO_4 etc.

Base: NaOH, KOH, $Ba(OH)_2$ etc.

Salt: NaCl, KCl, $CaCl_2$, KNO_3, $CuSO_4$ etc.

Weak Electrolytes: These are the substances which dissociate to a small extent in aqueous solution and hence conduct electricity also to a small extent.

Examples:

Acids: H_2CO_3, CH_3COOH, HCN etc.

Base: NH_4OH, $Al(OH)_3$, $Zn(OH)_2$ etc.

Salt: $MgCO_3$, $PbCl_2$, $BaCO_3$ etc.

3.3. Degree of ionization

As we know that the weak electrolytes do not ionize completely, so an equilibrium will reach between the ionized and unionized species in the solution. The degree of ionisation may be defined as the fraction of total amount of a weak electrolyte that exists in the ionized form. It is denoted by a Greek letter 'α'.

$$\text{So,} \quad \alpha = \frac{\text{Number of molecules dissociated at equilibrium}}{\text{Total number of molecules taken}} \qquad (1)$$

Consider a weak electrolyte AB, which dissociates in water and forms A^+ and B^-. So an equilibrium will be established in solution.

Let the initial concentration of the weak electrolyte, AB is c mol/L and α is the degree of dissociation. Then at equilibrium the concentration of A^+ and B^- will be αc mol/L and concentration of AB will be (c- αc) mol/L.

	AB $\rightleftharpoons$	A^+ +	B^-
Initial concentration:	c	0	0
Equilibrium concentration:	$c(1-\alpha)$	αc	αc

So according to the law of mass action the equilibrium constant can be written as

$K = \frac{[A^+][B^-]}{[AB]}$ where K is the dissociation constant or ionization constant.

$$\text{So,} \quad K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha} \qquad (2)$$

As for a weak electrolyte $\alpha << 1$; we can take $(1 - \alpha) = 1$.

$$K = \alpha^2 c \quad \text{or,}\ \alpha = \sqrt{\frac{K}{c}} \qquad (3)$$

So if we know the value of the dissociation constant of the weak electrolyte and the concentration of the weak electrolyte we can find its degree of dissociation or ionization.

Factors affecting degree of ionization:

The degree of ionization of a weak electrolyte depends on the following factors:

1. **Nature of electrolytes:** The degree of ionization depends upon the nature of electrolytes. Strong electrolytes have a high degree of ionization (value of á is equal to 1) while weak electrolytes have a low degree of ionization.
2. **Nature of solvent:** The ionizing power of the solvent depends upon its dielectric constant. The greater the value of the dielectric constant greater will be ionizing power of solvent and the greater will be the degree of ionization.
3. **Dilution:** From equation 3, we can observe that degree of ionization is inversely proportional to the concentration i.e. $\alpha \propto \frac{1}{\sqrt{c}}$. This is known as the Ostwald's dilution law. So, the degree of ionization increases with an increase in dilution. At infinite dilution, even the weak electrolytes are almost completely ionized.
4. **Temperature:** The degree of ionization increases with the increase in temperature.

5. **Common ion effect:** Due to the common ion effect, the degree of ionization of weak electrolytes is decreased or suppressed. The suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having common ion is called common ion effect.

3.4. Ionization of weak acids and bases

Ionization of weak acid:

Weak acids are dissociated to a very small extent in the solution and the ions produced on dissociation are in equilibrium with the undissociated molecules in solution

If HA represents any weak acid, we can write the dissociation reaction as,

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

and the corresponding dissociation constant expression as,

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (4)$$

K_a is the dissociation constant of the acid. If the initial concentration of the acid is c and α is the degree of dissociation, then the equilibrium concentrations would be,

	HA ⇌	H^+	+ A^-
Initial concentration:	c	0	0
Equilibrium concentration:	$c(1-\alpha)$	αc	αc

Substituting these values in equation 4, we get

$$K_a = \frac{\alpha^2 c}{1-\alpha} \qquad (5)$$

for a weak acid á << 1; we can take $(1 - \alpha) = 1$.

$$\alpha = \sqrt{\frac{K_a}{c}} \qquad (6)$$

From this equation we can calculate the degree of dissociation of a weak acid.

Now the concentration of H^+ ion in the solution can be calculated using equation 6

$$\left[H^+\right] = \alpha c = \sqrt{\frac{K_a}{c}} \times c = \sqrt{K_a c} \qquad (7)$$

Ionization of weak base:

Similarly for a weak base BOH, we can write the dissociation reaction as,

$$BOH \rightleftharpoons B^+ + OH^-$$

and the corresponding dissociation constant expression as,

$$K_b = \frac{\left[B^+\right]\left[OH^-\right]}{[BOH]} \qquad (8)$$

K_b is the dissociation constant of the weak base. If the initial concentration of the base is c and α is the degree of dissociation, then the equilibrium concentrations would be,

	$BOH \rightleftharpoons$	B^+	+ OH^-
Initial concentration:	c	0	0
Equilibrium concentration:	$c(1-\alpha)$	αc	αc

Substituting these values in equation 8, we get

$$K_b = \frac{\alpha^2 c}{1-\alpha} \qquad (9)$$

for a weak base $\alpha \ll 1$; we can take $(1 - \alpha) = 1$.

$$\alpha = \sqrt{\frac{K_b}{c}} \qquad (10)$$

From this equation we can calculate the degree of dissociation of a weak base.

Now the concentration of OH^- ion in the solution can be calculated using equation 10

$$\left[OH^-\right] = \alpha c = \sqrt{\frac{K_b}{c}} \times c = \sqrt{K_b c} \qquad (11)$$

3.5. Ionization constant and ionic product of water

Pure water is poor conductor of electricity. This shows that water is weak electrolyte i.e., it is ionized to a very small extent as

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (12)$$

or $$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (13)$$

Although eqs. 12 and 13 are representations of the same equilibrium, eq. 13 is a better representation in the sense that a free proton having a high charge density and extremely small size is incapable of free existence in solution and, therefore, gets attached to a molecule of water. However, since our calculations on equilibrium constant will not be different in case of either representation, for simplicity sake, we represent the water equilibrium by eq 12.

Applying law of chemical equilibrium, its dissociation constant K, is given by

$$K = \frac{\left[H^+\right]\left[OH^-\right]}{\left[H_2O\right]} \qquad (14$$

$$K[H_2O] = [H^+]\ [OH^-] \qquad (15)$$

In pure water the concentration of H_2O molecules is approximately 55.4 M and since the dissociation of H_2O is negligibly small in comparison with its concentration, we can safely assume that the concentration of H_2O at equilibrium is a constant quantity. Thus, K $[H_2O]$ in eq. 15 can be replaced by a new constant.

$$K_w = [H^+]\ [OH^-] \qquad (16)$$

where K_w is called the dissociation constant of water or, more commonly, the ionic product of water. Hence ionic product of water may be defined as the product of the molar concentration of H^+ and OH^- ions.

The value of K_w at 298 K (25 ^{0}C) is experimentally determined as $K_w = 1.0 \times 10^{-14}$.

Hence, $[H^+]\ [OH^-] = 1.0 \times 10^{-14}$ (17)

Since the amount of H^+ and OH^- produced by the dissociation of pure water is equal, concentration of each ion in solution is given by

$$\left[H^+\right]\left[OH^-\right] = \sqrt{K_W} = 1.0 \times 10^{-7} \quad \text{(for pure water} \qquad (18)$$

Like any equilibrium constant, K_w also depends on temperature as with increase of temperature degree of dissociation of water increases. So the concentration of H^+ and OH^- also increases. The following table shows the variation of K_w with temperature.

T(°C)	K_w (mol^2 dm^6)
0	0.114×10^{14}
25	1.008×10^{14}
50	5.476×10^{14}
100	51.3×10^{14}

3.6. pH scale

From the above discussion we have seen that the equilibrium of water is given by equation 14

$$K = \frac{\left[H^+\right]\left[OH^-\right]}{\left[H_2O\right]}$$

Now suppose that we add a small quantity of an acid to water, thereby increasing the concentration of H' ions at equilibrium. The equilibrium will immediately shift back to oppose the effect of this increase by the combination of the added H^+ ions with some OH^- ions to form undissociated water till eq.14 is satisfied. Once the equilibrium is re-established, the concentration of the hydrogen ion will be more than the concentration of the hydroxyl ion in solution. Hence, at 298 K, whenever the concentration of hydrogen ion in water is greater than 1.0×10^{-7} M, we call the solution to be acidic and whenever it is less than 1.0×10^{-7} M, we call it a basic solution. It is quite inconvenient to express these concentrations by using powers of 10. In 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called pH scale) for expressing the concentrations of H^+ ions. He defined pH as the negative logarithm of the molar concentration of hydrogen ions. That is,

$$pH = -\log_{10}[H^+] \qquad (19)$$

$$[H^+] = 10^{-pH} \qquad (20)$$

where H^+ ion concentration is expressed in mol dm^{-3}. The concept of negative logarithm can be used for defining the concentration of other ions also. For example, pOH represents the concentration of OH^- ion in solution and pM represents the concentration of the metal ion, M, in solution.

Pure water, where H^+ ion and OH^- ion concentration are both equal to 1.0×10^{-7} (at 298 K), will thus have a pH value of 7. An acidic solution means that the pH should be less than 7 and a basic solution should have pH greater than 7.

Let us consider a few simple calculations to see quantitatively as to what happens to the self-ionisation equilibrium of water when we add a small quantity of a strong acid to it. Consider a solution containing 0.010 mole of HCl in one dm^3 of water. The concentration of hydrogen ion due to HCl will be 1.0×10^{-2} M. This addition of acid will disturb the water equilibrium and this equilibrium will shift to left so that dissociation of water is suppressed. Thus, the concentration of H^+ ions produced by the self-ionisation of water ($\approx 10^{-7}$ M) is negligible in comparison with the H^+ ion produced by the added acid (10^{-2} M). Hence, the contribution due to water dissociation can be neglected in such a case and the pH of the solution will be 2. The concentration of OH^- will then be given by,

$$\left[OH^-\right] = \frac{K_W}{[H]^+} = \frac{1\times10^{-14}}{1\times10^{-7}} = 1\times10^{-12}$$

or $\qquad pOH = 12$

We can state this in a different way that, in 10^{-2} M acid solution, the concentration of OH^- ion (10^{-12} M in the above example) is less than the concentration of H^+ ion (10^{-2} M) and, the product of the two is always constant, and is equal to 1.0×10^{-14}.This can be expressed as,

$$pH + pOH = 14 = -\log K_w \qquad (21)$$

Thus, in pure water or a dilute solution of an acid or a base, we can express the concentration of H^+ or OH^- by simply stating the pH of the solution. We have also studied that the contribution due to self-ionisation of water is negligible in cases of solution of strong acids and bases as well as of moderately concentrated solutions of weak acids and weak bases. However, dealing with very dilute solutions of weak acids and bases, we cannot neglect the contributions due to self-ionisation equilibrium of water.

3.7. Common ion effect

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

Let us consider the dissociation of a weak acid such as acetic acid,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

the equilibrium constant for which can be represented as,

$$K_a = \frac{\left[H^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]} \tag{22}$$

or,
$$\left[H^+\right] = K_a \frac{\left[CH_3COOH\right]}{\left[CH_3COO^-\right]} \tag{23}$$

Now, suppose that we add some acetate ions in the form of solid sodium acetate to the above solution. Sodium acetate is added in the solid form so as not to cause any change in the volume of the solution. Sodium acetate being a strong electrolyte will dissociate almost completely to give Na^+ ions and CH_3COO^- ions in solution. The acetate ions so added will disturb the equilibrium of acetic acid. The equilibrium will, therefore, shift to left producing more of undissociated acetic acid in order to counteract the effect of added acetate ions according to Le Chatelier's principle. The net result is that the dissociation of the acid has been suppressed by the addition of a common ion (acetate ion in this case) at equilibrium. Thus any ion which is involved in a chemical equilibrium and comes from two different sources in solution is known as 'common ion' and its effect finds great use in the study of buffer solutions and the solubility of sparingly soluble salts which we will discuss in the next few sections.

3.8. Salt Hydrolysis - Hydrolysis Constant, Degree of Hydrolysis and pH for Different Salts

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

(i)	Salt of strong acid and strong base	(eg. HCl + NaOH)	NaCl
(ii)	Salt of strong acid and weak base	(e.g. HCl + NH_4OH)	NH_4Cl
(iii)	Salt of weak acid and strong base	(e.g. CH_3COOH + NaOH)	CH_3COONa
(iv)	Salt of weak acid and weak base	(e.g. CH_3COOH + NH_4OH)	CH_3COONH_4

Let us consider the acid base behaviour of the different type of salts.

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

(ii) Salt of strong acid and weak base: the salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid. For example,

NH_4Cl dissociates as:

$$NH_4Cl\ (aq) \rightarrow NH_4^+\ (aq)\ Cl^-\ (aq)$$

The anion from the strong acid does not get hydrolysed but the cation get hydrolysed as per the following equation:

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

which produces a weak base and excess of hydrogen ions in solution, thus rendering the solution acidic. Hence, we can say that the salt of a weak base and a strong acid will produce an acidic solution.

Let c mol/litre is concentration of the NH_4Cl and h is its degree of hydrolysis, then

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Initial concentration:	c	0	0
Equilibrium concentration:	c(1- h)	h c	h c

Therefore, according to law of mass action at equilibrium

$$K = \frac{[NH_4OH]\left[H^+\right]}{\left[NH_4^+\right][H_2O]}$$

or, $$K \times [H_2O] = \frac{[NH_4OH]\left[H^+\right]}{\left[NH_4^+\right]}$$

or, $$K_h = \frac{[NH_4OH]\left[H^+\right]}{\left[NH_4^+\right]} \qquad (24)$$

where K_h is the hydrolysis constant of salt NH_4Cl or NH_4^+ ion. Also we have for weak base NH_4OH which will get dissociate in water as

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{[NH_4OH]} \qquad (25)$$

From equation 24 and 25 we can write

$$K_h \times K_b = [H^+]\ [OH^-] = K_w$$

So, $$K_h = \frac{K_w}{K_b} \qquad (26)$$

From this equation we can calculate the hydrolysis constant.

Now from equation 24 we can get

$$K_h = \frac{[NH_4OH]\left[H^+\right]}{\left[NH_4^+\right]} = \frac{ch \times ch}{(1-h)c} = \frac{h^2c}{1-h} = h^2c$$

As h is very small so, (1-h) = 1

Hence, $$h = \frac{K_h}{c} = \sqrt{\frac{K_w}{K_b.c}} \qquad (27)$$

From this equation we can calculate the degree of hydrolysis of the salt.

Now, $$[H^+] = hc = \sqrt{\frac{K_w}{K_b.c}} \times c = \sqrt{\frac{K_w.c}{K_b}}$$

or, $$-\log\left[H^+\right] = -\frac{1}{2}\log K_w - \frac{1}{2}\log c + \frac{1}{2}\log K_b$$

or, $$pH = -\frac{1}{2}\log 10^{-14} - \frac{1}{2}\log c - \frac{1}{2}pK_b$$

or $$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log c \qquad (28)$$

This is the equation for the pH of a solution of salt of strong acid and weak base.

(iii) Salt of weak acid and strong base: the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. For example, CH_3COONa dissociates as:

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

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

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

So in the solution there will be excess OH- ion. Hence the salts of a weak acid and a strong base, when dissolved in water, will produce a basic solution.

By considering the similar method as above we can show that if c mol/litre is the concentration of the CH_3COONa and h is its degree of hydrolysis then

We can get

$$K_h = \frac{K_w}{K_a} \qquad (29)$$

$$h = \sqrt{\frac{K_w}{K_{a.c}}} \tag{30}$$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log c \tag{31}$$

(iv) Salt of weak acid and weak base: the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to a weak base. For example, ammonium acetate, CH_3COONH_4 dissociates as:

$CH_3COONH_4\ (aq) \rightarrow NH_4^+\ (aq) + CH_3COO^-\ (aq)$

In this case both the cation as well as the anion would undergo hydrolysis according to the following equations

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

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

Hydrolysis of one ion gives hydrogen ions, whereas that of the other ion gives hydroxyl ions in solution. Therefore, the pH of the solution will depend on the extent of the hydrolysis of the two ions. If NH_4^+ hydrolyses to a greater extent than CH_3COO^- ion, the solution will be acidic and, if the reverse is true, then the solution will be basic. If the extent of hydrolysis is exactly equal, then the solution should be neutral as if no hydrolysis is taking place.

By considering the similar method we can establish that if c mol/litre is the concentration of the CH_3COONH_4 and h is its degree of hydrolysis then

We can get

$$K_h = \frac{K_w}{K_a K_b} \tag{32}$$

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}} \tag{33}$$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b \tag{34}$$

From the equation 34, we can see that the pH of the solution is independent of the concentration of the salt.

If $pK_a = pK_b$ then the pH of the solution is 7.

When $pK_a \gg pK_b$ then the $pH > 7$, so the solution will be basic.

When $pK_a \ll pK_b$ then the $pH < 7$, so the solution will be acidic.

3.9. Buffer solutions

In section 3.7 we have seen that that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids / bases and a salt of common ion are important in a yet another way. These act as buffer solutions.

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

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

There are two kinds of commonly used buffer-solutions

i) A weak acid and a soluble ionic salt of the weak acid forms a buffer with pH less than 7 are called acidic buffers e.g. acetic acid and sodium acetate.

ii) A weak base and a soluble ionic salt of the weak base forms a buffer with pH above 7 are called basic buffers. e.g. ammonium hydroxide and ammonium chloride.

Let us consider a buffer solution containing acetic acid, CH3COOH and sodium acetate CH_3COONa to understand about how buffer resist the change of pH in the solution. In acetic acid - sodium acetate buffer CH_3COOH acts as acid reserve while CH_3COONa (or CH_3COO^- ions) works as the base reserve. In the solution mixture the added components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation.

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$

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

If we add a strong acid such as HCl to this solution, it produces H_3O^+. These added H_3O^+ (acid) react with an equivalent amount of the base reserve [CH_3COO^-] to generate undissociated acetic acid. The reaction being

$CH_3COO^-\ (aq) + H_3O^+\ (aq) \rightarrow CH_3COOH\ (aq) + H_2O\ (l)$

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

$CH_3COOH\ (aq) + HCl\ (aq) \rightleftharpoons CH_3COOH\ (aq) + NaCl\ (aq)$

Similarly, when small amount of a strong base like NaOH is added, it generates OH^- ions. These additional OH^- neutralize some of the H_3O^+ ions present in the solution. Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of CH_3COOH to re-establish the equilibrium. The net result is the neutralization of OH- by CH_3COOH. In other words we can say that the added OH^- ions (base) react with the acid reserve to produce CH_3COO^- ions.

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

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

$NaOH\ (aq) + CH_3COOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)$

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

So we can observe that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the hydronium ions and thereby the pH does not change significantly.

Now the pH of a buffer solution can be calculated from the Henderson's equation. Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid – sodium acetate buffer the central equilibrium is

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$

which is characterized by the acid dissociation constant,

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]}$$

Rearranging, we get

$$\left[H_3O^+\right] = K_a \frac{\left[CH_3COOH\right]}{\left[CH_3COO^-\right]}$$

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

$$\left[H_3O^+\right] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

Taking logarithm and multiplying by (-1) in both side we get

$$-\log\left[H_3O^+\right] = -\log K_a - \log\frac{[\text{Acid}]}{[\text{Salt}]}$$

or $$pH = pK_a - \log\frac{[\text{Acid}]}{[\text{Salt}]}$$

or, $$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad (35)$$

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

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \qquad (36)$$

3.10. Solubility and Solubility Product of Sparingly Soluble Salts

When a solute is added gradually to an amount of solvent, at a particular temperature, there comes a point when no more solute can be dissolved. This point gives a saturated solution. A solution which remains in contact with undissolved solute is said to be saturated. At the saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

Consider in general, the electrolyte of the type A_xB_y which is dissociated as:

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Applying law of mass action we can write

$$K = \frac{\left[A^{y+}\right]^x \left[B^{x-}\right]^y}{\left[A_xB_y\right]} \qquad (37)$$

When the solution is saturated,

$$[A_xB_y] = K' \text{ (constant)}$$

So we can write the equation 37 as

$$[A^{y+}]^x\,[B^{x-}]^y = K[A_xB_y] = K.K' = K_{sp} \text{ (constant)} \qquad (38)$$

K_{sp} is the solubility product constant or simply solubility product. Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times, the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

Relationship between solubility and solubility product:

Salts like AgI, $BaSO_4$, $PbSO_4$, PbI_2, etc. are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolytes contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, i.e., it is completely dissociated.

The equilibrium for a saturated solution of a sparingly soluble salt A_xB_y of solubility S mol/L may be expressed as:

A_xB_y (s) $\rightleftharpoons$ xA^{y+} (aq) + yB^{x-} (aq)

At equilibrium, $[A^{y+}] = xS$ mol/L and $[B^{x-}] = yS$ mol/L

So, $K_{sp} = [A^{y+}]^x\ [B^{x-}]^y = [xS]^x\ [yS]^y = x^x.\ y^y.\ (S)^{x+y}$ (39)

Special Cases:

(i) 1: 1 type salts: Examples: AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

$K_{sp} = S.S = S^2$

(ii) 1: 2 or 2: 1 type salts: Examples: Ag_2CO_3, Ag_2CrO_4, $PbCl_2$, CaF_2, etc.

$K_{sp} = S.(2S)^2 = 4S^3$

(iii) 1: 3 type salts: Examples: AlI_3, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$,etc.

$K_{sp} = S.(3S)^3 = 27S^4$

Example 1. At 298 K, the solubility of silver chloride is 1.37 x 10^{-5} M. Calculate its solubility product.

Solution: The equilibrium of silver chloride is AgCl $\rightleftharpoons$ $Ag^+ = Cl^-$

Here x= 1 and y = 1, So, $K_{sp} = S^2 = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$

Effect of common ion on solubility of sparingly soluble salt:

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

Let us extend the problem in example 1 as, what will be the solubility of AgCl in 0.01 M $AgNO\text{-}_3$ solution?

Addition of 0.01 M concentration of $AgNO_3$ will provide 0.01 M of Ag^+ ions in the solution as $AgNO_3$ is a strong electrolyte. Assuming this contribution to be much larger in comparison with Ag^+ ion concentration due to dissolved AgCl (solubility S mol/L), we can write.

$[Ag^+] = 0.01$ and $[Cl^-] = S$

So, $K_{sp} = 1.88 \times 10^{-10} = [Ag^+][Cl^-] = 0.01 \times S$

or, $S = 1.88 \times 10^{-8}$

We can see that, as compared to the solubility of AgCl in water (1.37×10^{-5} M), its solubility in presence of 0.01 M $AgNO_3$ is almost 10^3 times less.

Application of solubility product in qualitative analysis:

The qualitative analysis of cations is carried out by dividing them into several groups. This group separation of cations is based upon selective precipitation of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the K_{sp} of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of H_2S. The dissociation of H_2S can be written as

$$H_2S\ (aq) \rightleftharpoons 2H^+\ (aq) + S^{2-}\ (aq)$$

Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions. We know that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the S^{2-} ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out.

3.11. Summary

In summary we have started the discussion explaining electrolytes and non electrolytes. Then we focused our discussion on strong and weak electrolytes followed by degree of dissociation for weak electrolytes and the factors affecting the degree of dissociation. Ionization of weak acid and weak bases are discussed. After that, ionic product of water was explained and the concept was extended for establishing the concept of pH scale. We have found the effect of common ion in dissociation of weak acid and bases. We have learned about the salt hydrolysis and calculated the hydrolysis constant, degree of hydrolysis and pH for different types of salts. We have seen that the presence of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called Henderson's equation. After that we have discussed that the product of the concentration of the ions in the solubility equilibrium is a constant called solubility product (K_{sp}) and is proportional to the solubility of the sparingly soluble salt. We have found that the presence common ion decreases the solubility of a sparingly soluble salt. This is called common ion effect and has widespread applications in qualitative analysis.

3.12. Questions

1. Write a short note on pH scale.
2. What is degree of ionization?
3. What are sparingly soluble salts?
4. What will happen if we pass HCl gas in a saturated solution of NaCl?
5. What is buffer? Give example of one acidic and one basic buffer.
6. Why the pH of a buffer remains constant upon addition of small amount of acid or base?
7. Why the solution of $FeCl_3$ is acidic?
8. If the solubility of Zinc phosphate in water is S mol/L, then find the expression for the solubility product of the salt. (Ans. 108 S^5)
9. Calculate the pH of 0.1 M NaOH solution. (Ans. 13)
10. If in 1 L of buffer solution 0.2 mol of NH_4Cl and 0.1 mol of NH_4OH is dissolved then what will be the pH of the solution? Given that K_b of NH_4OH is 1.8×10^{-5}. (Ans. 8.96)

Unit 4 ❐ Kinetic Theory of Gases

Contents

4.0. Objectives

After studying this unit, we will be able to:

- state the postulates of kinetic theory of gases
- derive the kinetic gas equation $PV = \frac{1}{3} mnc^2$
- explain the distribution of molecular speeds and energies
- calculate the most probable speed, the average speed and the root mean square speed
- derive an expression to calculate the collision number between gas molecules
- calculate the mean free path of molecules
- explain the origin and factors responsible for viscosity of gases

- differentiate between ideal gas and real gas and reasons for deviation from ideal behaviour
- explain the critical phenomenon and critical constants.

4.1. Introduction

The kinetic theory describes a gas as a large number of sub microscopic particles (atoms or molecules), all of which are in constant, and random motion. The rapidly moving particles constantly collide with each other and with the walls of the container. Kinetic theory explains macroscopic properties of gases, such as pressure, temperature, viscosity, thermal conductivity, and volume, by considering their molecular composition and motion. The theory depicts that gas pressure is due to the impacts, on the walls of a container, of molecules or atoms moving at different velocities.

4.2. Postulates of kinetic theory of gases

The kinetic molecular theory of gases explains the laws that describe the behaviour of gases. This theory developed during the mid-19th century by several physicists, including the Boltzmann, Clausius and Maxwell. The kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following postulates:

i. Every gas consists of large number of tiny particles called point masses i.e. the actual volume of molecules is negligible when compared to the total volume of the gas.

ii. The gas molecules are always in a state of rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel.

iii. A molecule moves in a straight line with uniform velocity between two collisions.

iv. The molecular collisions are perfectly elastic so that there is no net loss of energy when the gas molecules collide with one another or against the walls of the vessel.

v. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one another.

vi. The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained.

vii. The average kinetic energy of gas molecules is directly proportional to absolute temperature.

viii. This means that the average kinetic energy of molecules is the same at a given temperature.

4.3. Kinetic gas equation

Suppose a definite amount gas is placed in a cubic closed vessel of length l. Let the mass of the each gas molecule is m. The gas consists of total n molecules and each molecule is moving randomly with a velocity c (root mean square velocity). This velocity c can be divided into three components of u, v and w along X, Y and Z direction respectively.

$$c^2 = u^2 + v^2 + w^2$$

Now, we consider the movement of a molecule along X axis (figure 4.1). If the velocity of the molecule along X axis is u then the momentum is momentum is mu. Now when the molecule collides perpendicular to the wall of the container with velocity u, it will revert back to the opposite direction with same velocity as the collision is an elastic collision. The velocity after the collision will be –u. As the collision between the molecules and walls are elastic, so the momentum will be same before and after the collision. So the change in momentum after a collision with the wall = mu- (-mu) = 2mu

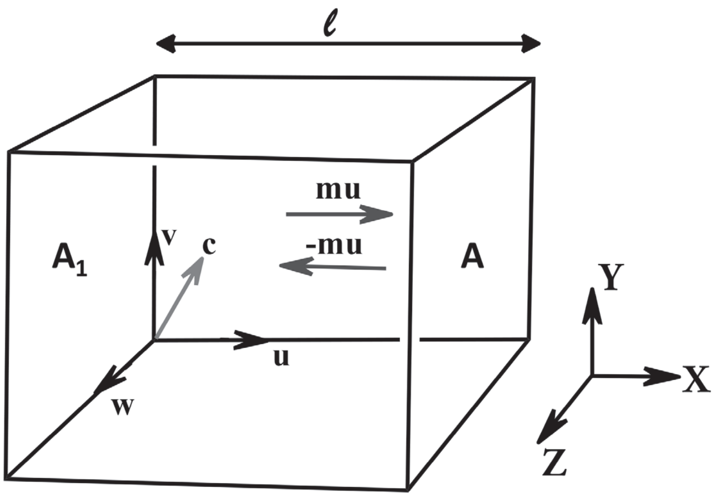


Figure 4.1. Velocity of a gas molecule along X-axis placed in a cubic container.

Now after collision with the A side of the wall it will reflect and will collide with the opposite wall at a distant of ℓ.

Hence, the number of collision per second for a gas molecule moving along X-axis with a velocity $u = \frac{u}{l}$

So for u component of velocity of a molecule change in momentum per second

$$= \frac{u}{l} \times 2mu = \frac{2mu^2}{l}$$

For the same molecule the change of momentum per second for the v and w component of the velocity will be $\frac{2mv^2}{l}$ and $\frac{2mw^2}{l}$ respectively.

Total change of momentum for a molecule per second

$$= \frac{2mu^2}{l} + \frac{2mv^2}{l} + \frac{2mw^2}{l}$$

$$= \frac{2m}{l}\left(u^2 + v^2 + w^2\right) = \frac{2mc^2}{l}$$

For n number of molecules rate of change of momentum $= \frac{2mnc^2}{l}$

From the Newton's second law we know that rate of change of momentum is equal to the force. As the pressure (P) is equal to the force acting per unit area and the total surface area of the container = $6l^2$.

So we can write, $P = \frac{2mnc^2}{l} \times \frac{1}{6l^2} = \frac{2mnc^2}{6l^3} = \frac{2mnc^2}{6V} = \frac{1}{3} \cdot \frac{mnc^2}{6V}$

$$\text{or,} \qquad PV = \frac{1}{3} mnc^2 \tag{1}$$

This is known as kinetic gas equation.

4.4. Maxwell Boltzmann distribution laws of molecular velocities and molecular energies

In a given mass of gas, the velocities of all molecules are not the same, even when bulk parameters like pressure, volume and temperature are fixed. Collisions change the direction and the speed of molecules. However in a state of equilibrium, the distribution of speeds is constant or fixed. If at a particular temperature T, dN_c number of molecules are present in between the velocity c and (c + dc) among total N number of molecules then the Maxwell's equation of distribution of molecular velocity is given by the following equation-

$$\frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc \qquad (2)$$

Where, dN_c is the number of molecules having velocity between c to c + dc, m is the mass of the each gas molecule, N is the total number of gas molecules present, k is Boltzmann constant and T is absolute temperature of the gas. Also the equation can be written as

$$\frac{dN_c}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2RT}} c^2 dc \qquad (3)$$

Where R = universal gas constant, M = Molecular weight of the gas.

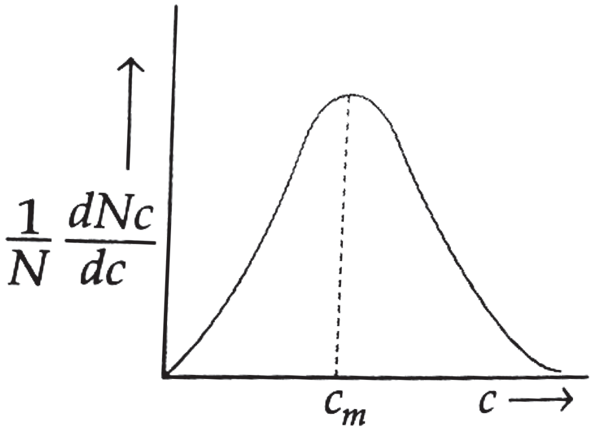


Figure 4.2. Plot of Maxwell's distribution of molecular velocities.

The Maxwell distribution is customarily plotted with the function $\frac{1}{N}\frac{dN_c}{dc}$ in the y-axis and c as the x-axis. The fraction of the molecules in the speed range c to c + dc is $\frac{dN_c}{dc}$; dividing this by dc gives the fraction of the molecules in this speed range per unit width of the interval. The Maxwell's distribution of molecular velocities is plotted in figure 4.2.

We can see from the plot that the fraction of molecules having velocities greater than zero increases with an increase in velocity, reaches a maximum and then falls off towards zero at higher velocities. The important features of the curves are as follows:

i) The fraction of molecules with too low or too high velocities is very small.

ii) There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity.

Effect of temperature on distribution of molecular velocities for a particular gas:

Effect of temperature on distribution of molecular velocities for a N_2 gas is plotted in figure 4.3. The important features are:

i) The entire distribution curve shifts to the right and becomes broader with increase in temperature

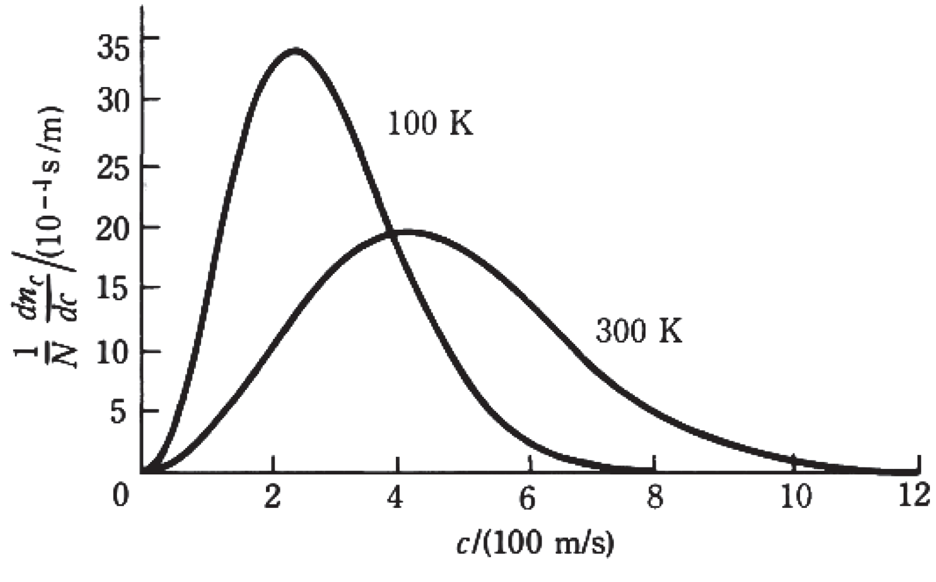


Figure 4.3. Maxwell distribution for nitrogen at two temperatures.

ii) With increase of temperature fraction of the molecules having high velocities increases considerably.

iii) The most probable velocity increases with increase in temperature but the number of molecules present at that velocity decreases.

Distribution of molecular energies:

The Maxwell's speed distribution, eq. 2, can be converted to an energy distribution. The kinetic energy of a molecule is $\varepsilon = \frac{1}{2}mc^2$. Then, $c = \left(\frac{2}{m}\right)^{\frac{1}{2}} \varepsilon^{\frac{1}{2}}$. Thus equation 2 can be converted to energy distribution equation as

$$\frac{dN_\varepsilon}{N} = 2\pi N\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon \qquad (4)$$

where dN_ε, is the number of molecules having kinetic energies between ε and ε +dε.

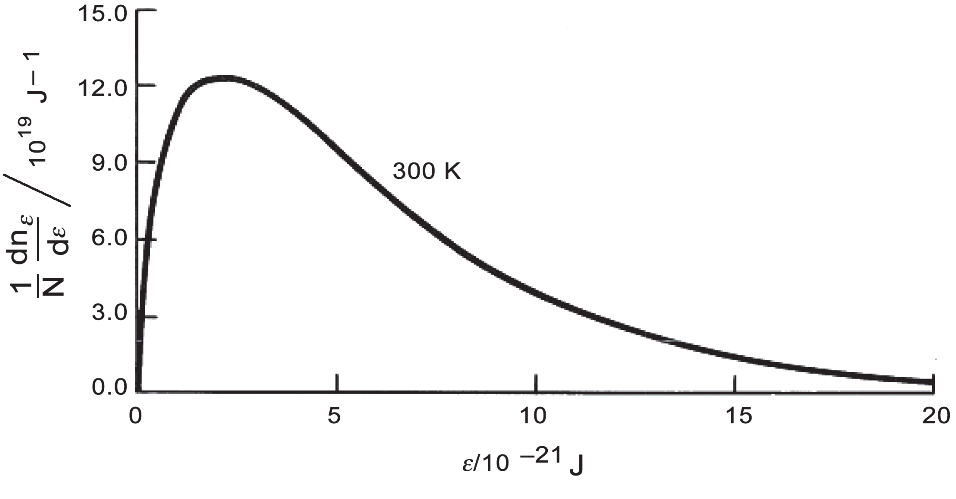


Figure 4.4. Energy distribution at 300 K.

Energy distribution curve is distinctly different shape compared to that of the speed distribution (figure 4.4). In particular, the energy distribution curve rises sharply at the beginning and thus it rises much more quickly than the velocity distribution. After passing the maximum, the energy distribution falls off more slowly than does the velocity distribution. As usual, the distribution is broadened at higher temperatures, a greater proportion of the molecules having higher energies. As before, the areas under the curves for different temperatures must be the same.

4.5. Average, root mean square and most probable velocities

Mean or Average velocity (C_{av})

The average speed is the sum of all the velocities ranging from 0 to " divided by total number of molecules present (n). If for a gas n_1, n_2, n_3..... number of molecules has the velocity of c_1, c_2 c_3... respectively then the average velocity will be

$$c_{av} = \frac{n_1c_1 + n_2c_2 + n_3c_3 + ...}{n_1 + n_2 + n_3 + ...} = \frac{\sum n_ic_i}{n}$$

From Maxwell's equation of distribution of velocity, it can be shown that the average velocity for a gas with molecular mass M is

$$C_{av} = \sqrt{\frac{8RT}{\pi M}} \qquad (5)$$

where, R is universal gas constant and T is temperature of the gas.

Root Mean Square Velocity (C_{rms})

The root mean square velocity or rms velocity is the square root of the sum of all the squared velocities ranging from 0 to ∞ divided by total number of molecules N.

If for a gas n_1, n_2, n_3..... number of molecules has the velocity of c_1, c_2 c_3... respectively then the root mean square velocity of the gas molecules will be

$$C_{rms} = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ...}{n_1 + n_2 + n_3 + ...}} = \sqrt{\frac{\sum n_ic_i^2}{n}}$$

From Maxwell's equation of distribution of velocity, it can be shown that the root mean square velocity for a gas with molar mass M at temperature T is

$$C_{rms} = \sqrt{\frac{3RT}{M}} \qquad (6)$$

Most Probable Velocity (C_{mp})

The most probable velocity is the velocity possessed by maximum number of molecules at a particular temperature.

From Maxwell's equation of distribution of velocity, it can be shown that the most probable velocity (c_{mp}) for a gas with molar mass M at temperature T is

$$C_{mp} = \sqrt{\frac{3RT}{M}} \qquad (7)$$

4.6. Collision parameters

Collision diameter:

The kinetic theory of gases treats molecules as point masses. When two such molecules approach each other, a point is reached at which the repulsion between the molecules (resulting from electronic and nuclear repulsion) becomes so strong that it causes reversal of the direction of their motion. The distance between the centres of the two molecules at the point of their closest approach is known as collision diameter (σ). Evidently, a gaseous molecule can be regarded as a hard sphere of radius 'σ/2'. It can be imagined that if the distance between the centres of two molecules is less than σ, there would be a collision between them. Thus, collision is an event in which the centres of two identical molecules come within a distance between d from each other.

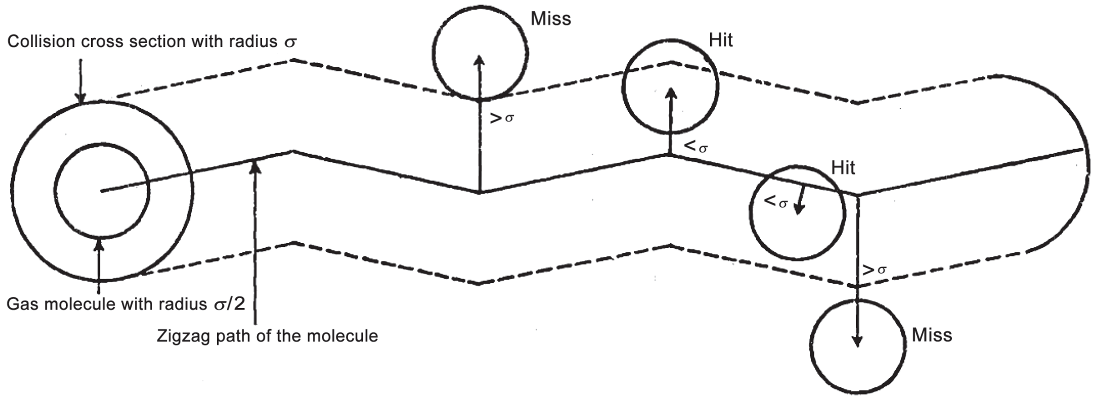


Figure 4.5. The zigzag motion of a gas molecule.

Collision cross section:

The model of gaseous molecules as hard non-interacting spheres of diameter σ can satisfactorily account for various gaseous properties such as viscosity, diffusion, thermal conductivity, mean free path, number of collision the molecules undergo. It can be imagined that when two molecules collide, the effective area of the target is $\pi\sigma^2$. The quantity $\pi\sigma^2$ is called the collision cross-section of the molecule because it is the cross-sectional area of an imaginary sphere surrounding the molecule into which the centre of another molecule cannot penetrate.

Collision number:

Collision number is the number of collisions suffered by a single molecule per unit time per unit volume of the gas. It can be imagined that a gas molecule having diameter σ will collide with the molecules present in the area of $\pi\sigma^2$. Now if the molecule is moving with an average velocity of $\langle c \rangle$ and n′ number of molecules are present in unit volume then in one second total number of collisions suffered by the molecule will be $\pi\sigma^2 \cdot \langle c \rangle \cdot n'$. Now as all the gas molecules are moving this velocity should be considered as relative velocity $\left(\sqrt{2}\langle c \rangle\right)$. So, the number of molecules with which a single molecule will collide per unit time is given by $Z_1 = \sqrt{2}\pi\sigma^2 \langle c \rangle n'$. This is the expression of collision number.

Now as n′ number of molecules are present per unit volume of the gas, total number of collisions per unit time per unit volume is = $\sqrt{2}\pi\sigma^2 \langle c \rangle n'^2$. Since each collision involves two molecules, the number of collisions of like molecules occurring per unit time per unit volume of the gas is given by

$$Z_{11} = \frac{1}{2}\left(\sqrt{2}\pi\sigma^2 \langle c \rangle n'^2\right) = \frac{1}{\sqrt{2}}\pi\sigma^2 \langle c \rangle n'^2 = \frac{1}{\sqrt{2}}\pi\sigma^2 n'^2 \cdot \sqrt{\frac{8RT}{\pi M}}$$

$$\left(\text{as} \langle c \rangle = \frac{8RT}{\pi M}\right)$$

$$Z_{11} = 2\sigma^2 n'^2 \cdot \sqrt{\frac{8RT}{\pi M}}$$

This number Z_{11} represent the number of molecular collisions occurring per unit time per unit volume of the gas, which is known as collision frequency.

Mean free path of molecules:

Mean free path of a gas molecule (ℓ or λ) is defined as the mean distance travelled by a gas molecule between two successive collisions.

Now we already know that if a molecule has the average velocity $\langle c \rangle$ then the molecule will face $Z_1 = \sqrt{2}\pi\sigma^2 \langle c \rangle n'$ number of collisions while travelling $\langle c \rangle$ distance.

So, Mean free path,

$$l = \frac{\text{average velocity of the molecule}}{\text{number of collisions per second}} = \frac{\langle c \rangle}{\sqrt{2}\pi\sigma^2 \langle c \rangle n'} = \frac{1}{\sqrt{2}\pi\sigma^2 n'}$$

where, σ = collision diameter and n' = number of molecules present per unit volume.

4.7. Viscosity of gases

The viscosity of a fluid is a measure of its resistance to deformation at a given rate. Viscosity can be conceptualized as quantifying the internal frictional force that arises between adjacent layers of fluid that are in relative motion. Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The viscosity coefficient (η) is the force that must be applied to hold the lower layer stationary if the velocity gradient between the two layers is unity and the plate has unit area. It can be shown from the kinetic theory that the relation between viscosity coefficient (η) and mean free path (ℓ) of a gas molecule can be given by the following equation-

$\eta = \frac{1}{3} m n' \langle c \rangle l$ where, $\langle c \rangle$ is average velocity, n' is the number of gas molecules present in unit volume and m is the mass of the gas molecules.

Effect of temperature and pressure on coefficient of viscosity:

Effect of pressure: The viscosity of gas is independent of pressure. With increase of pressure though more number of molecules changes between the layers, but they travel shorter distance due to higher number of collisions. So the change of pressure does not affect the viscosity for gases.

Effect of temperature: Viscosity in gases arises from molecules traversing layers of flow and transferring momentum between layers. The momentum transfer is caused by free motion of gas molecules between collisions. So, increase of thermal agitation of the molecules results in a larger viscosity. Hence, gaseous viscosity increases with increase of temperature.

We know, $l = \frac{1}{\sqrt{2}\pi\sigma^2 n'}$ and $\eta = \frac{1}{3} mn' \langle c \rangle l$

So, $\eta = \frac{1}{3} mn' \langle c \rangle l \times \frac{1}{\sqrt{2}\pi\sigma^2 n'} = \frac{1}{3} \cdot \frac{m\langle c \rangle}{\sqrt{2}\pi\sigma^2} = \frac{1}{3} \cdot \frac{m}{\sqrt{2}\pi\sigma^2} \cdot \sqrt{\frac{8kT}{\pi m}} = \frac{2}{3\sigma^2} \cdot \sqrt{\frac{mkT}{\pi^3}}$ (9)

From the above equation we can see that, $\eta \propto \sqrt{T}$

4.8. Deviation of real gases from ideal behaviour

We know that ideal gases obey ideal gas equation (PV = RT, for one mole gas) at any pressure and temperature. But real gases do not obey ideal gas equation under all conditions. They nearly obey ideal gas equation at higher temperatures and very low pressures. However they show deviations from ideality at low temperatures and high pressures.

Compressibility factor and Boyle temperature:

The deviations of real gases from ideal behaviour are best represented in terms of the compressibility factor (Z). Compressibility factor is the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. It correlates the deviation of a real gas from ideal gas behaviour. To display the deviations clearly, the ratio of the observed molar volume $\overline{V}$ to the ideal molar volume $\overline{V}_{id}$ (= RT/P) is plotted as a function of pressure at constant temperature. This ratio is called the compressibility factor (Z = PV/RT).

For the ideal gas, Z = 1 and is independent of pressure and temperature. For real gases Z is a function of both temperature and pressure. The graphs plotted for the compressibility factors determined for a number of gases over a range of pressure at a constant temperature are shown in Figure 4.6. At extremely low pressure all the gases are known to have Z close to unity which means that the gases behave almost ideally. At very high pressure, all the gases have Z is greater than unity indicating that the gases are less compressible than an ideal gas. This is due to the fact that at high pressure, the molecular repulsive force is dominant. At moderately low pressure carbon monoxide, methane and ammonia are more compressible than ideal gas (Z<1). The compressibility factor Z goes on decreasing with increase of pressure passes through a minimum at a certain stage and then begins to increase with increase in pressure for these gases. For hydrogen and helium, Z is greater than unity (the ideal value) at all pressures.

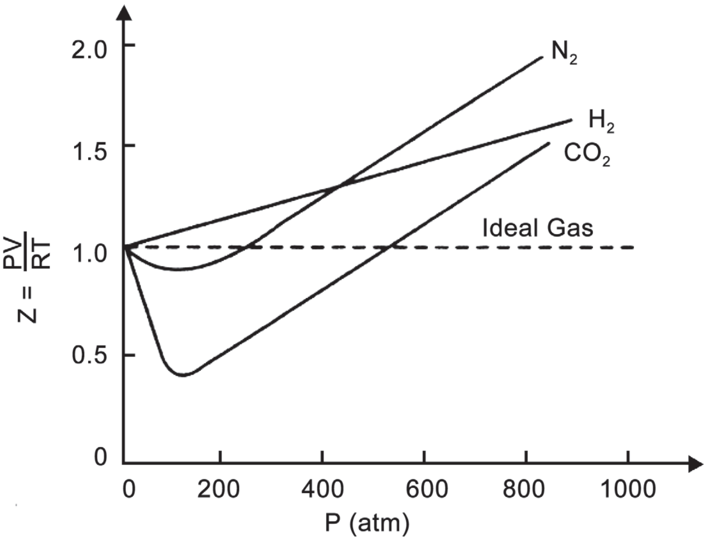


Figure 4.6. Compressibility factor Z, plotted against pressure for H_2, N_2 and CO_2 at constant temperature.

From the plot of plot of Z versus p (figure 4.7) for nitrogen at different temperatures varying between -70°C and 50°C it is seen that as the temperature is raised the dip in

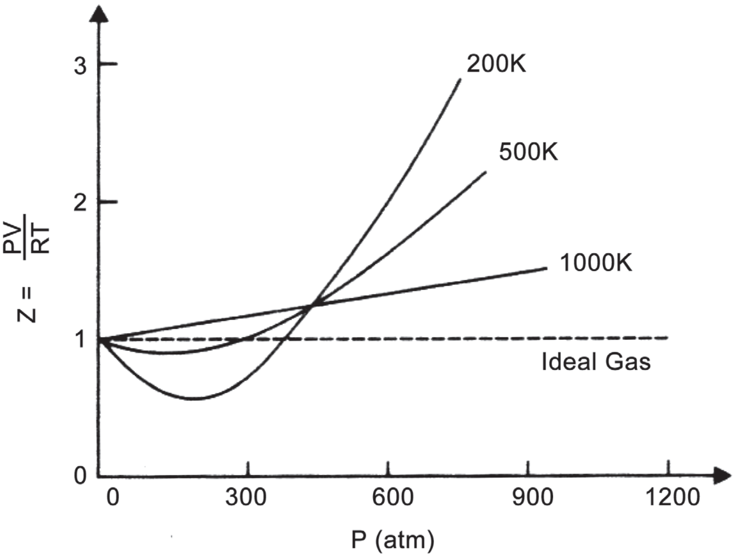


Figure 4.7. Plot of Z against P at different temperature for N_2.

the curve becomes smaller and smaller. At 50°C, the curve seems to remain almost horizontal (Z=1) at the low pressure region. So it can be said that at this region PV remain constant and thus it obeys the Boyle's law within this range of pressure at 50°C. This temperature is called Boyle temperature. The Boyle temperature is different for different gases.

Causes of deviation and Van der Waals equation of state for real gases:

In order to explain deviations from ideal behaviour, it is necessary to modify the kinetic theory of gases. Van der Waals realized that two of the assumptions of the kinetic molecular theory were questionable. The kinetic theory assumes that gas particles occupy a negligible fraction of the total volume of the gas. It also assumes that the force of attraction between gas molecules is zero.

The first assumption works at pressures close to 1 atm. But something happens to the validity of this assumption as the gas is compressed. Imagine for the moment that the atoms or molecules in a gas were all clustered in one corner of a cylinder. At normal pressures, the volume occupied by these particles is a negligibly small fraction of the total volume of the gas. But at high pressures, this is no longer true. As a result, real gases are not as compressible at high pressures as an ideal gas. The volume of a real gas is therefore larger than expected from the ideal gas equation at high pressures.

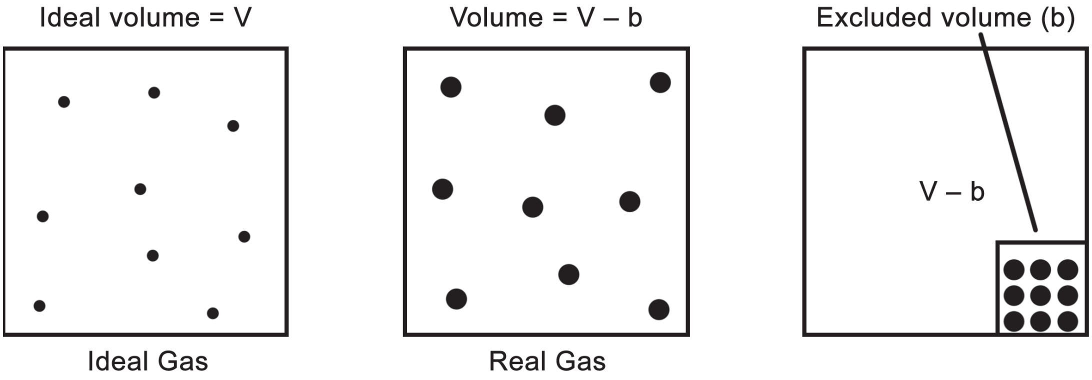


Figure 4.8. Excluded volume in case of real gas.

Van der Waals proposed that we correct for the fact that the volume of a real gas is too large at high pressures by subtracting a term from the volume of the real gas before we substitute it into the ideal gas equation. He therefore introduced a constant (b) into the ideal gas equation that was equal to the volume actually occupied by a mole of gas particles. Because the volume of the gas particles depends on the number of moles of gas in the container, the term that is subtracted from the real volume of the gas is equal to the product of number of moles of gas and *b*.

$$P(V - nb) = nRT$$

When the pressure is relatively small, and the volume is reasonably large, the nb term is too small to make any difference in the calculation. But at high pressures, when the volume of the gas is small, the nb term corrects for the fact that the volume of a real gas is larger than expected from the ideal gas equation.

The assumption that there is no force of attraction between gas particles cannot be true. If it was, gases would never condense to form liquids. In reality, there is a small force of attraction between gas molecules that tends to hold the molecules together. This force of attraction has two consequences: (i) gases condense to form liquids at low temperatures and (ii) the pressure of a real gas is sometimes smaller than expected for an ideal gas.

To correct for the fact that the pressure of a real gas is smaller than expected from the ideal gas equation, van der Waals added a term to the pressure in this equation. This term contained a second constant (a) and has the form: n^2a/V^2. The complete **van der Waals equation** is therefore written as follows.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \qquad (10)$$

This is the van der Waals equation for n moles of gas which contains a pair of constants ‘a’ and ‘b’. The’ quantities ‘a’ and ‘b’ are called the van’der Waals constants or parameters. It may be pointed that *‘b’* is a measure of the molecular size and ‘a’ is related to the intermolecular interaction. The SI unit of a is N m^4 mol^{-2} and the unit of b is m^3 mol^{-1}.

4.9. Critical phenomena

When the molecules of a gas are brought closer to each other due to increase in the attractive forces a stage may be reached when the gas changes its phase to liquid. Obviously, an ideal gas cannot be liquefied as there are no interactions in that case. For the liquefaction of real gases, we can do either of the following: i) increase the pressure on the gas or ii) decrease the temperature of the gas. Both these processes will tend to bring the molecules closer and liquefaction may take place. But it is observed practically that temperature is the dominant factor for liquefaction and pressure assumes a secondary role. For every real gas a temperature is observed above which it cannot be liquefied even on the application of very high pressures. This characteristic temperature of a real gas above which it cannot be liquefied is called "Critical Temperature" represented by T_C.

The importance of critical temperature of a gas was first discovered by Andrew in his experiments on pressure-volume relationships (isotherms) of carbon dioxide gas at a series of temperatures. The isotherm of carbon dioxide determined by him at different temperatures is shown in figure 4.9.

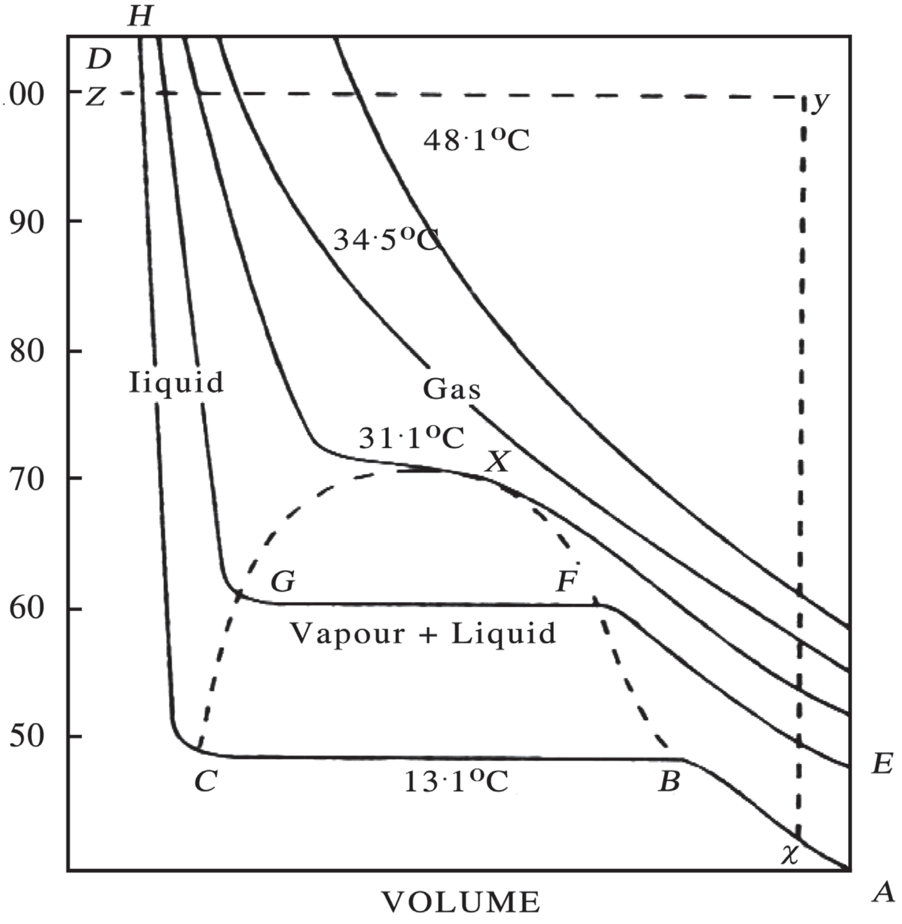


Figure 4.9. P-V isotherms of carbon dioxide.

We observe from the plot that:

i. At high Temperatures (>31.1°C), the isotherms look just like those of ideal gas.

ii. At low temperatures the curve is entirely different. For example, curve ABCD at temperature 13.1°C, as the pressure increases the volume of the gas decreases from point A to B. Then there is a sudden reduction in volume without much increase in pressure of the gas from B to C. In this portion liquefaction is taking place at constant pressure and due to the difference in the properties of gas and liquid the volume is reducing so much. And after C even on increasing pressure there is no appreciable decrease in volume as now only liquid is present. So, AB represents gaseous phase, BC represents liquid-gas coexistence and CD represents liquid phase.

iii. On carrying out the same process at a higher temperature we observe that the width of the horizontal portion decreases and the pressure at which liquefaction takes place also becomes higher. The horizontal portion decreases because at higher temperatures the properties of liquid approach that of a gas.

iv. At temperature 31.1°C (T_C) the horizontal portion reduces to a mere point at which liquefaction takes place. Point X is called critical point; at this point the boundary between liquid and gas phase (meniscus) disappears indicating that both the phases have identical characteristics.

v. Above this temperature there is no liquefaction of gases and gas behaves almost ideally.

At critical point X the tangent is horizontal, so that, dP/dV at critical point will be zero. Thus, the point X is also called the point of deflection.

Critical constants:

Critical temperature, T_C is the maximum temperature at which a gas can be liquefied that is a temperature above which liquid cannot exist.

Critical Pressure, P_C is the minimum pressure required for liquefaction to take place at the critical condition.

Critical volume, V_C is the volume occupied by one mole of the gas at critical temperature and critical pressure.

It can be shown that the values of these parameters are given by the following expressions:

$$T_C = \frac{8a}{27Rb}$$

$$P_C = \frac{a}{27b^2}$$

$$V_C = 3b$$

where R is the universal gas constant.

These critical constants are related by the following relation

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} \qquad (11)$$

4.10. Summary

In this unit, we have discussed some characteristic microscopic features of gases. It has been shown how a simple kinetic molecular model of the gas can be used to derive an equation to calculate the pressure exerted by a gas. This equation can be used further to derive the ideal gas equation. This model is useful in showing how the constant collisions between molecules are responsible for a distribution of the speed of molecules. Further, this model helps us in deriving expressions for various kinds of speeds. We have also evolved a method of calculating the total collision frequency and the mean free path assuming hard sphere model for the molecules. We have discussed the viscosity of gases and effect of temperature on the viscosity. The deviation of real gas from ideal behaviour was explained and van der Waals equation was derived. Finally the critical phenomenon and critical constants were explained for real gases.

4.11. Questions

1. Write down the postulates of kinetic theory of gases.
2. Derive the expression of pressure for an ideal gas using kinetic molecular theory of gases.
3. Write down the expression for Maxwell distribution of molecular velocities.

4. What is mean free path of a gas? What is the relation between mean free path and collision diameter?
5. How does the viscosity of gas vary with temperature?
6. What is compressibility factor of a gas?
7. What are the reasons for deviation of real gases from ideal behaviour?
8. Write down the definitions of critical constants.
9. Calculate the average velocity of CO_2 molecule present in 1 gm of CO_2 gas at 27 ^{0}C. (Ans. 3.8×10^4 cm/s)
10. If $T_C = 304.2$ K and $P_C = 72.8$ atm for a gas, then calculate the value of va der Walls constants. (Ans. $a = 3.63$ atm L^2 mol^{-2}, $b = 0.0428$ L mol^{-1})

Unit 5 ❒ Liquids

Contents

5.0. Objectives

After studying this unit, we will be able to

- the surface tension and origin of surface tension of a liquid
- effect of temperature in the surface tension
- determine the surface tension of a liquid
- explain the viscosity of a liquid and effect of temperature on viscosity
- determine the viscosity by using Ostwald viscometer.

5.1. Introduction

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases. Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as surface tension and viscosity.

5.2. Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid? Why does an iron needle float in the water? All these phenomena are caused due to the characteristic property of liquids, called surface tension.

If we consider the forces between the molecules of a liquid then we can understand these phenomena easily. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecules therefore do not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Figure 5.1), due to the molecules below it, since there are no molecules or very less number of molecules as vapour above it. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, liquids tend to have minimum number of molecules at their surface. A sphere has a minimum surface for a given volume. As a result of the tendency to contract, surface of a liquid behaves as if it were in a state of tension. The force that tends to contract the surface of a liquid is known as surface tension.

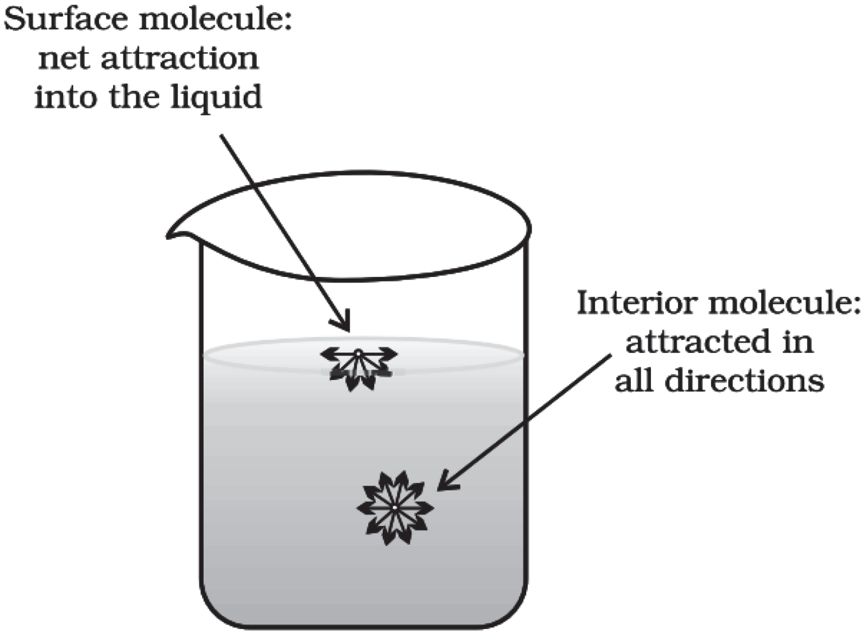


Figure 5.1. Forces acting on a molecule on liquid surface and on a molecule inside the liquid.

Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is represented by Greek letter γ (Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as Nm^{-1}.

Surface Energy: The effect of surface tension is to reduce the area of the surface to a minimum. If we wish to increase the area of the surface of a liquid, we have to work against the force of surface tension. The energy required to increase the surface area of the liquid by one unit is defined as surface energy of the liquid. Its SI unit is Jm^{-2}.

Effect of Temperature on Surface Tension: The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

Some Effects of Surface Tension: Some important effects can be explained by surface tension.

1. Due to presence of surface tension in liquids every liquid try to reduce the area of the surface to a minimum. Hence drops of a liquid or the drops of rain are spherical in shape as sphere has minimum surface area for a given volume.

2. As the surface of a liquid tries to contract due to tension, so it behaves like a membrane. Also the distances between the surfaces of molecules are less. So an iron needle can float in the water.

3. Capillary action of a liquid is a well known phenomenon which can be explained in terms of surface tension. If the liquid in the glass tube is water, the water is drawn slightly up the walls of the tube by adhesive forces between water and glass. The interface between the water and the air above it, called a *meniscus*, is concave, or curved in. With liquid mercury, the meniscus is convex, or curved out. Cohesive forces in mercury, consisting of metallic bonds between Hg atoms, are strong; mercury does not wet glass. The effect of meniscus formation is greatly magnified in tubes of small diameter, called *capillary tubes*. In the *capillary action*, the water level inside the capillary tube is noticeably higher than outside. The soaking action of a sponge depends on the rise of water into capillaries of a fibrous material, such as cellulose. The penetration of water into soils also depends in part on capillary action. Conversely, mercury- with its strong cohesive forces and weaker adhesive forces- does not show a capillary rise. Rather, mercury in a glass capillary tube will have a lower level than the mercury outside the capillary.

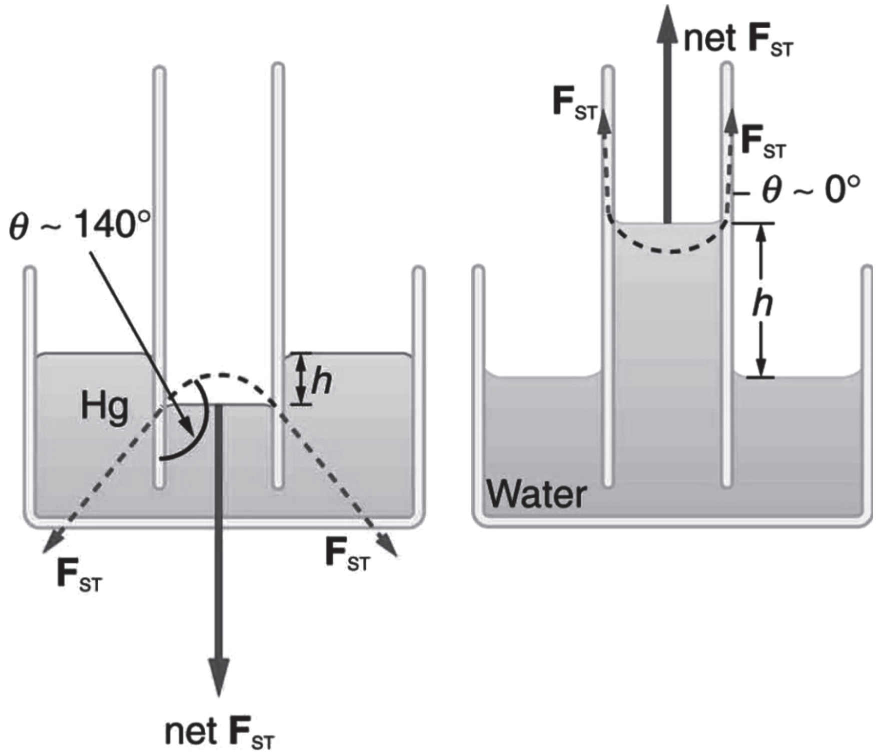


Figure 5.2. Capillary action of liquid.

4. When a drop of liquid spreads into a film across a surface, we say that the liquid *wets* the surface. Whether a drop of liquid wets a surface or retains its spherical shape and stands on the surface depends on the strengths of two types of intermolecular forces. The forces exerted between molecules holding them together in the drop are **cohesive forces**, and the forces between liquid molecules and the surface are **adhesive forces**. If cohesive forces are strong compared with adhesive forces, a drop maintains its shape. If adhesive forces are strong enough, the energy requirement for spreading the drop into a film is met through the work done by the collapsing drop. Water wets many surfaces, such as glass and certain fabrics. This characteristic is essential to its use as a cleaning agent. If glass is coated with a film of oil or grease, water no longer wets the surface and water droplets stand on the glass. Adding a detergent to water has two effects: The detergent solution dissolves grease to expose a clean surface, and the detergent lowers the surface tension of water. Lowering the surface tension means lowering the energy required to spread drops into a film. Substances that reduce the surface tension of water and allow it to spread more easily are known as w*etting agents*. They are used in applications ranging from dish washing to industrial processes.

5.3. Determination of surface tension using Stalagmometer

Stalagmometer is a simple apparatus and is frequently employed when the values of surface tension of two or more different liquids are to be compared. It consists of a bulbed capillary tube, the end of which is flattened and grounded carefully so that there is a large dropping surface. There are two marks, A and B, on the wall of it which are arbitrarily etched; one of them is above the bulb and the other is below the bulb. A liquid is sucked up to the level A and then allowed to flow at a slower rate drop by drop until it reaches the level B. The speed of the drop formation can be adjusted by attaching a piece of rubber tube with a screw pinch cock at the upper end of the tube.

When a liquid is allowed to flow through a capillary tube, a drop begins to form at its lower end, and increases in size to a certain extent, and then falls off. The size of the drop will depend on the radius of the capillary and the surface tension of the liquid. The total surface tension supporting the drop is $2\pi r\gamma$, where r is the outer radius of the capillary tube, see Fig. 5.3 The drop will fall when its weight ‘w’, just exceeds the force of surface tension acting along the circumference. Therefore,

$$w = 2\pi r\gamma \qquad (1)$$

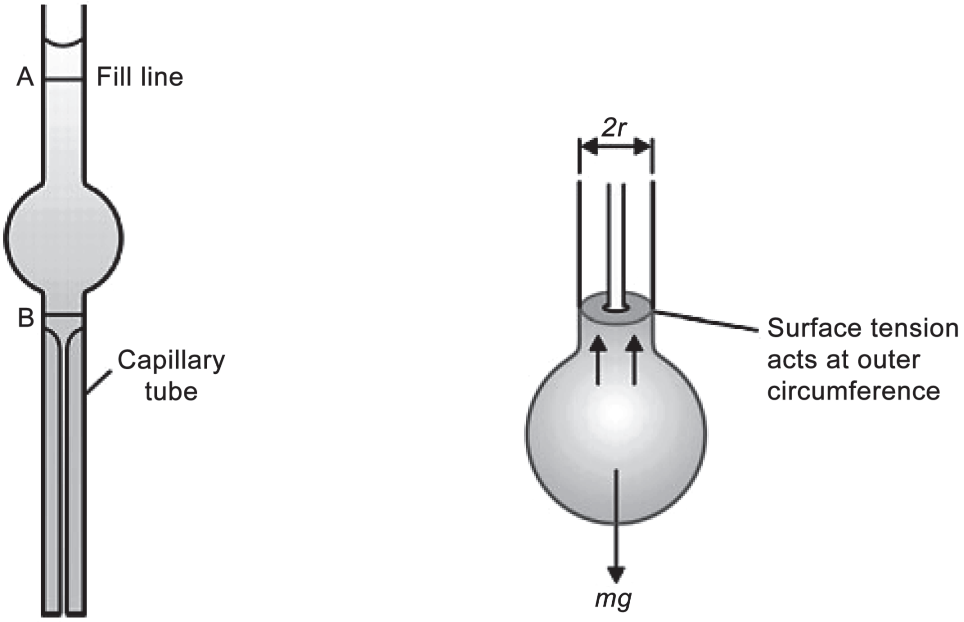


Figure 5.3. Drawing of a stalagmometer and the formation of liquid drop from a capillary tube in a stalagmometer.

where w, is the weight of the drop and $2\pi r$ is the outer circumference of the capillary tube.

From the above expression, it is clear that the surface tension of a liquid can be determined if the weight of a single drop 'w' and the outer radius of the dropping tube, 'r' are known.

If, we have two liquids, such that

$$w_1 = 2\pi r \gamma_1 \text{ and } w_2 = 2\pi r \gamma_2$$

then, we can say that $\frac{w_1}{w_2} = \frac{\gamma_1}{\gamma_2}$ (2)

If γ_1 for one of the liquids is known, γ_2 for other liquid can be determined without needing a measurement of r, the outer radius of the dropping end of the capillary, provided the weights of the individual drops of two liquids are known. This method of determination is also known as *Drop Weight Method***.** Alternatively, the surface tension can also be determined using the *Drop Number Method* as given below.

Instead of finding the weights of individual drops, it is easier to count the number of drops formed by equal volumes of two liquids. With two different liquids, the weights of equal volumes are proportional to their densities. If n_1 and n_2 are the number of drops formed by the same volume V of the two liquids, then; v_1, the volume of a single drop of first liquid (i.e., liquid one) = V/n_1.

Thus, weight of the single drop of the first liquid = $w_1 = V/n_1.d_1.g$, where d_1 is the density of the first liquid.

And the weight of the single drop of the second liquid = $w_2 = V/n_2.d_2.g$, where d_2 is the density of the second liquid.

Substituting the above values of w_1 and w_2 in equation 2, we get

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{V}{n_1} d_1 g}{\frac{V}{n_2} d_2 g} = \frac{\frac{d_1}{n_1}}{\frac{d_2}{n_2}} = \frac{n_2 d_1}{n_1 d_2} \tag{3}$$

where, γ_1 and γ_2 are the surface tensions of two individual liquids, and d_1 and d_2 are their densities, respectively. Thus, for the determination of surface tension of any liquid, the number of drops produced from equal volume of two liquids and their densities must be known, in addition to the surface tension of the reference liquid (e.g. water).

5.4. Viscosity of a liquid

Viscosity is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another. Viscosity can be defined as the force of friction between two layers of a liquid moving past one another with different velocities.

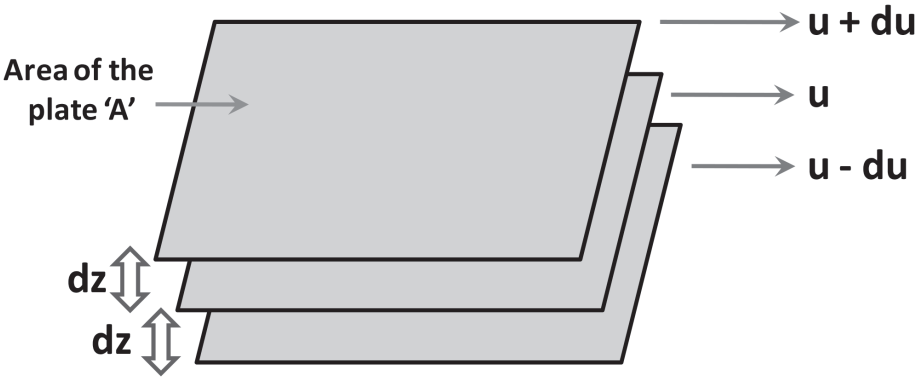


Figure 5.4. Gradation of velocity in the laminar flow.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow. If we choose any layer in the flowing liquid (Fig.5.4), the layer above it accelerates its flow and the layer below this retards its flow. If the velocity of the layer at a distance dz is changed by a value: 'du' then velocity gradient is given by the amount $\frac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \propto A$ (A is the area of contact)

$F \propto \frac{du}{dz}$ (where, $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$$F \propto A \cdot \frac{du}{dz}$$

$$F = \eta A \frac{du}{dz} \qquad (4)$$

'η' is proportionality constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 Newton second per square metre ($N\ s\ m^{-2}$) = pascal second ($Pa\ s = 1 kg\ m^{-1}s^{-1}$). In CGS system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

$$1 \text{ poise} = 1\ g\ cm^{-1}s^{-1} = 10^{-1}\ kg\ m^{-1}s^{-1}$$

Greater the viscosity, the more slowly the liquid flows. The viscosity is very much influenced by the shape, size and the chemical nature of the liquid molecules. The greater the size of the molecules and the higher the molar mass, the higher will be the viscosity because the greater will be the intermolecular interactions. The hydrogen bonds also enhance the coefficient of viscosity to a large extent. It is, indeed, the presence of a network of hydrogen bonds which accounts for the very high viscosity of glycerol. Incidentally, the larger the number of hydroxyl groups in a molecule, the more complex will be the network of hydrogen bonds and the greater will be the resistance of a liquid to flow. In long chain hydrocarbons or polymeric compounds the viscosity increases with the increase in the length of the molecular chain. Due to this reason, heavy hydrocarbon oil and grease (which are used as lubricants) have fairly high viscosity values.

Effect of Temperature on viscosity of Liquids:

In liquids, as the temperature raises, the kinetic energy of the molecules increases and the intermolecular forces of attraction become weak, resulting in the subsequent decrease in the viscosity. The value of the coefficient of viscosity appreciably drops as the temperature of liquid increases such that for each degree rise in temperature there is about two percent decrease in the viscosity. The viscosity and temperature are related to each other by the following expression:

$$\log \eta = \frac{A}{T} + B$$

where A and B are constants for a given liquid and T is the absolute temperature.

5.5. Determination of Coefficient of Viscosity using Ostwald Viscometer

For the measurement of coefficient of viscosity of liquids having a laminar or streamlined flow through a tube or pipe, Poiseuille derived an expression, known as Poiseuille's equation. This expression is given below.

$$\eta = \frac{\pi p r^4 t}{8Vl} \qquad (5)$$

where = coefficient of viscosity of the liquid

V = volume of the liquid flowing out of the tube

t = time in which the volume V flows

r = radius of the tube

1 = length of the tube

p = driving pressure necessary to maintain uniform rate of flow of volume V, of the liquid.

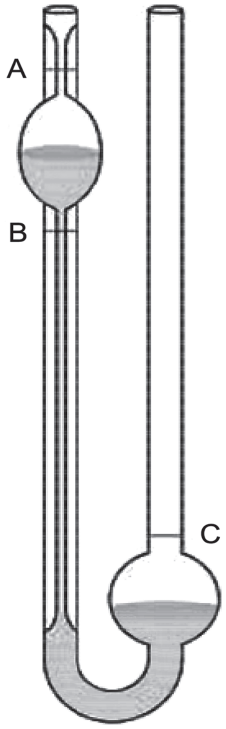


Figure 5.5. Diagram of a Ostwald viscometer.

This involves the use of Ostwald Viscometer (Figure 5.5) in which a fixed volume of a liquid is allowed to fall under its own weight or the force of gravity, and the time required for a given volume of the liquid to flow is noted. Obviously the driving pressure p is replaced by h.d.g, where h is the height of the liquid and d is its density and g is the acceleration due to gravity. Therefore,

$$p = h.d.g$$

Substituting h.d.g. for p in Poiseuille's Equation 5, we get,

$$\eta = \frac{\pi r^4.h.d.g.\,t}{8Vl} \qquad (6)$$

If equal volumes of the two liquids (1 and 2) are allowed to fall through the same capillary tube under identical conditions of temperature and pressure then, from Eq. 5.6 by comparison, we have

$$\frac{\eta_1}{\eta_2} = \frac{d_1.t_1}{d_2.t_2} \qquad (7)$$

where η_1, $d_1$and t_1 are, respectively, the coefficient of viscosity, density and time of flow for the liquid 1under examination and η_2, d_2 and t_2 the corresponding values for the reference liquid (liquid 2). Thus, by knowing η_2, d_2 , t_2 and d_1 and t_1 the coefficient of viscosity of first liquid, could be determined.

5.6. Summary

In this unit we have discussed about the characteristics of liquids. Surface tension and viscosity of liquids were explained and the dependence of these characteristics on intermolecular forces was highlighted. Also the theory behind experimental determination of surface tension and viscosity were discussed.

5.7. Questions

1. What is surface tension? How the surface tension of a liquid varies with Temperature?
2. What is surface energy? What is its unit?
3. Why the drop of a liquid is spherical?

4. Write down the theory for determination of surface tension using stalagmometer by drop count method.

5. Why the viscosity of water is higher than alcohol?

6. How viscosity coefficient of a liquid does vary with temperature?

7. Write down the theory for determination of viscosity of a liquid using Ostwald viscometer.

8. If 10 ml of water and ether forms 29 and 86 drops respectively in a viscometer at 293 K, then calculate the surface tension of ether. Given that surface tension of water is $7.2 \text{ x } 10^{-2}$ N/m and density of ether is 0.7 gm/cc at 293 K.

   (Ans. 1.6995×10^{-2} N/m)

9. In an Ostwald viscometer the flow time for water and toluene of equal volume is 102.2 second and 68.9 second respectively. Find out the viscosity coefficient of toluene if the viscosity coefficient of water is 0.01009 dyne s cm^{-2}.

   (Ans. 5.9 × 10-3 dyne s cm^{-2})

Unit 6 ❐ Solids

CONTENTS

6.0. Objectives

After studying this Unit, we will be able to

- describe general characteristics of solid state
- distinguish between amorphous and crystalline solids
- identify the symmetry elements in a solid
- define lattice, basis, unit cell, primitive and nonprimitve cells
- describe the seven crystal systems and the fourteen Bravais lattices

- state the laws of crystallography
- state the crystal planes in terms of Miller indices,
- state Bragg's law
- describe the structure of NaCl, KCl and CsCl
- describe the imperfections in solids and types of defects in a crystal

6.1. Introduction

We are mostly surrounded by solids and we use them more often than liquids and gases. For different applications we need solids with widely different properties. These properties depend upon the nature of constituent particles and the binding forces operating between them. In gaseous state we have studied that if thermal energy is much greater than the forces of attraction then we have matter in gaseous state. Molecules in gaseous state move with very large speeds and because of very small attraction forces, the gas molecules move practically independent of one another.

In the liquid state the forces of attraction are greater than the thermal energy. We have also studied that molecules in liquid state too have kinetic energy, they cannot move very far away because of the larger forces of attraction amongst them. Because of this property, liquids have definite volume, but they do not have definite shape. Liquids also resemble gases in their ability to flow. Gaseous and liquid states are, therefore, both classified as fluids.

The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them.

A true solid possesses the following characteristics

(a) A sharp melting point

(b) A characteristic heat of fusion

(c) General incompressibility

(d) A definite three-dimensional arrangement

Hence solids are characterised by high density and low compressibility compared to those of the gas phase. In solids, atoms, ions and molecules are held together by relatively strong chemical forces- ionic bond, covalent bond, or by intermolecular Van der Waal's forces. They do not translate although they vibrate to some extent on their fixed positions. This explains why solids are rigid and have definite shape.

6.2. Forms of solids

Solids can generally be classified into two broad categories:

(i) Crystalline solids

(ii) Amorphous solids

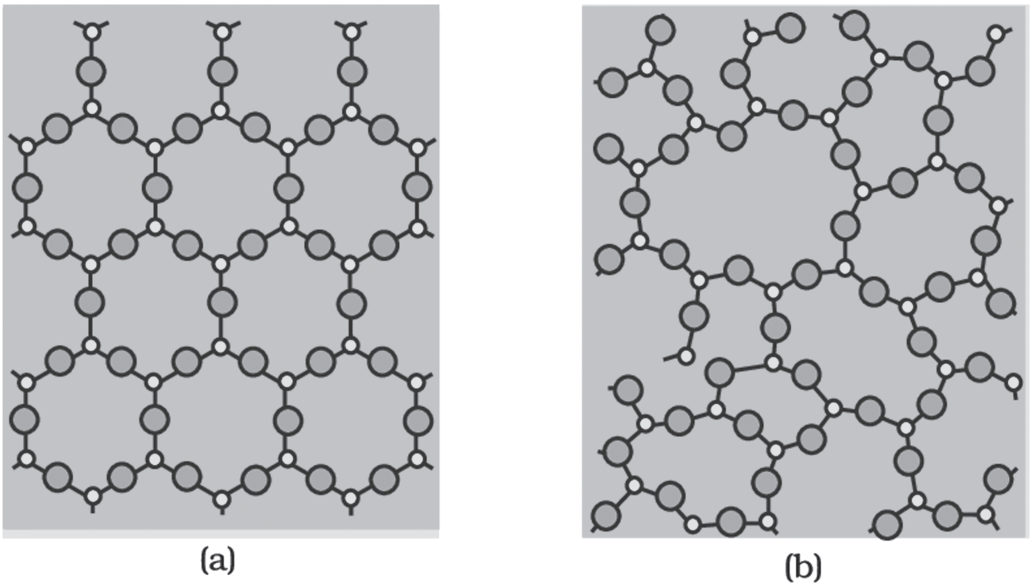


Figure 6.1. Two dimensional structure of (a) quartz and (b) quartz glass.

A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the crystal lattice. Examples of crystalline solids are sugar, salt, quartz etc. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only short range order. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered. Examples of amorphous solids are rubber, plastics and quartz glass. In their disordered structure, amorphous solids are regarded as super-cooled liquids with high viscosity. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 6.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no long range order.

Anisotropy and isotropy:

Amorphous substances differ from crystalline solids and resemble liquids in another important aspect. Their properties such as electrical conductivity, thermal conductivity mechanical strength and refractive index are same in all directions. Amorphous substances are said to isotropic. Liquids and gases are also isotropic.

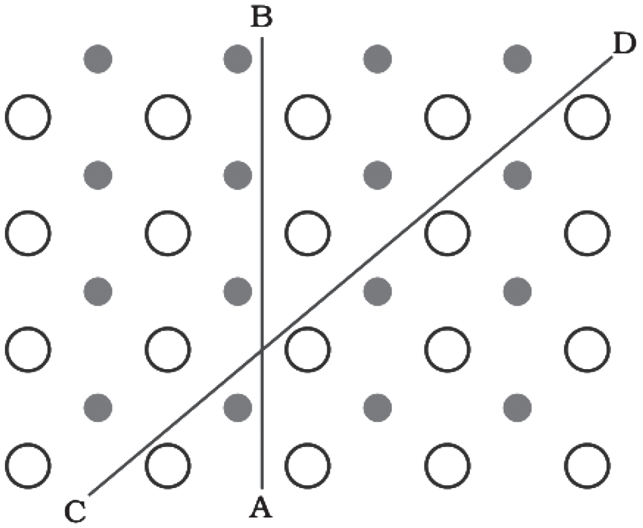


Figure 6.2. Anisotropy in crystals is due to different arrangement of particles along different directions.

Crystalline solids on the other hand are anisotropic, because their physical properties are different in different directions. For example the velocity of light through a crystal varies with the direction in which it is measured. Thus, a ray of light enter such a crystal may split up into two components each following different velocity. This phenomenon is known as double refraction. This can be shown in fig 6.2 in which simple two-dimensional arrangement of only two different kinds of atoms is depicted if the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case; each row is made up of one type of atoms only. In amorphous solids, atoms or molecules are arranged at random and in a disorderly manner and, therefore all directions are identical and all properties are alike in all directions.

6.3. Symmetry elements

In crystallography, symmetry is used to characterize crystals, identify repeating parts of molecules. An object is described as symmetric with respect to a transformation if the object appears to be in a state that is identical to its initial state, after the transformation. In crystallography, most types of symmetry can be described in terms of an apparent movement of the object such as some type of rotation or translation. The apparent movement is called the symmetry operation. The locations where the symmetry operations occur such as a rotation axis, a mirror plane or an inversion center are described as symmetry elements.

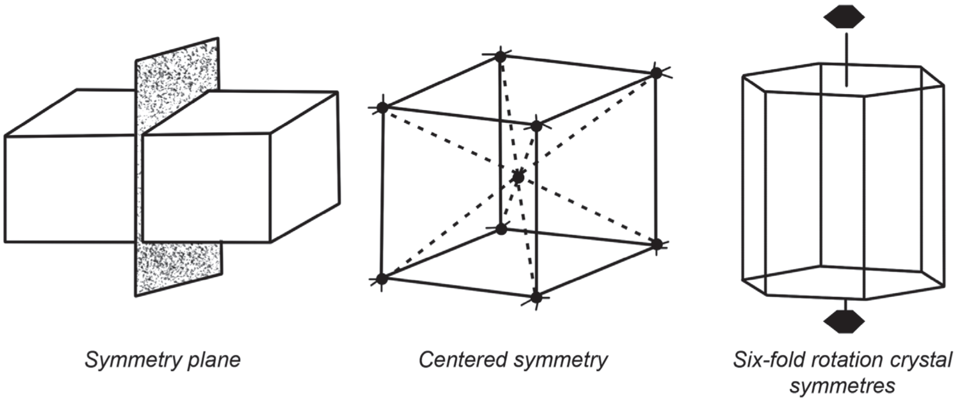


Figure 6.3. Symmetry elements.

Plane of symmetry

When an imaginary plane can divide by a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a plane of symmetry.

Axis of symmetry

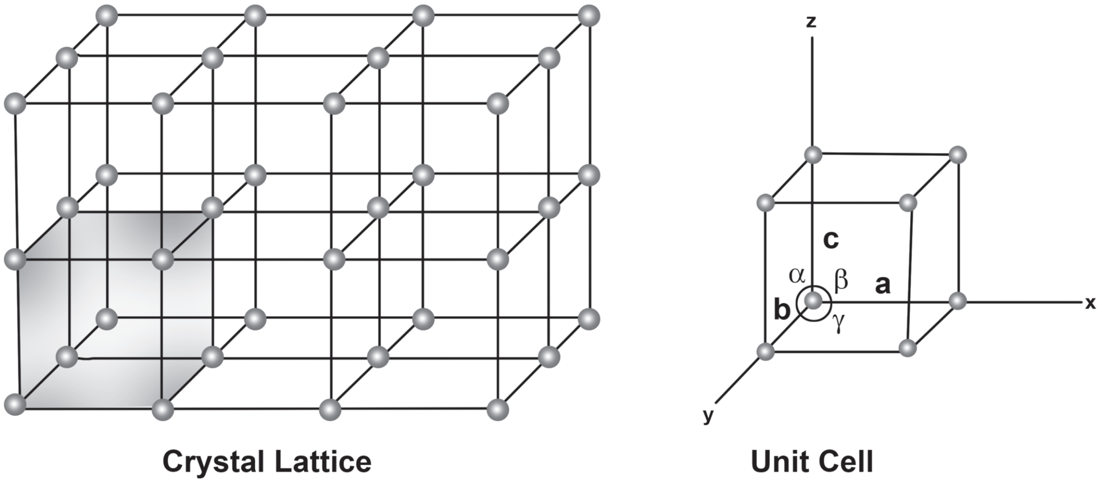
An axis of symmetry is a line about which the crystal is rotated such that it presents the similar appearance more than once during complete rotation i.e. rotation through an angle of 360^0. Depending upon its nature, a crystal may have 2-fold, 3-fold, 4-fold or 6-fold axes of rotation.

Centre of Symmetry

It is a found at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distance on either side. It may be pointed out that a crystal may have number of planes or axis of symmetry but it has only one centre of symmetry.

6.4. Unit cell

The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, a regular three dimensional arrangement of points in space is called a crystal lattice. A portion of a crystal lattice is shown in Fig. 6.4.



Crystal Lattice **Unit Cell**

Figure 6.4. Crystal lattice and unit cell of a solid.

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice. A unit cell is characterised by:

(i) its dimensions along the three edges, *a*, *b* and *c*. These edges may or may not be mutually perpendicular.

(ii) angles between the edges, α (between *b* and *c*) β (between *a* and *c*) and ã (between *a* and *b*). Thus, a unit cell is characterised by six parameters, *a, b, c,* α, β and γ.

Unit cells can be of following types;

(a) Simple or primitive unit cell (P): The simplest unit cell which has the lattice points at the corners is called a simple or primitive unit cell. It is denoted by P.

(b) Non primitive or multiple unit cell: When unit cell contains more than one lattice points, it is called non primitive or multiple unit cell. It is further divided into the following three categories:

(i) **Face centred unit cell (F):** When a unit cell, besides the points present at the corners of the unit cell, there is one point at the centre of each face, it is called face centred arrangement or face centred unit cell. It is denoted by F.

(ii) **Body centred unit cell (I):** When in a unit cell, besides the points at the corners of the cell, there is one point at the centre with in its body, it is called body-centred arrangement or body-centred with cell. It is denoted by I.

(iii) **Side centre or end face unit cell:** When in a unit cell, besides the points at the corners of the cell, the points are located at the centre of any two parallel faces of the unit cell, it is called side-centred or end face unit cell. It is denoted by c.

6.5. Crystal systems

It can be shown from geometrical considerations that, theoretically, there can be 32 different combinations of elements of symmetry of crystal. These are called 32 point

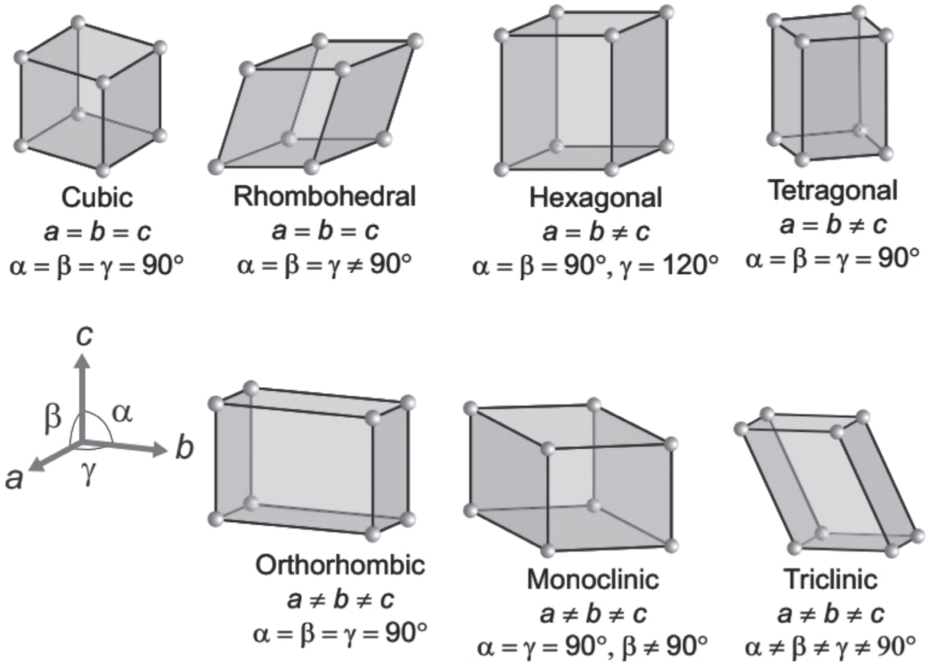


Figure 6.5. Seven crystal system.

group or 32 crystal systems. Some of the systems, however, have been grouped together so that we have only seven different categories, known as the seven basic crystal systems. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral or trigonal (figure 6.5). Crystal systems differ in length of the unit cell edges and the angles between the unit cell edges.

6.6. Bravais lattice types

These seven different kinds of crystal systems in combination with four different kinds of centerings (primitive, base-centered, body-centered, face-centered) can yield 14 distinct lattice types which are called Bravais lattices. However, not all of the combinations of crystal systems and centerings are unique; some of the combinations are equivalent while other combinations are not possible due to symmetry reasons. This reduces the number of unique lattices to the 14 Bravais lattices. The distribution of the 14 Bravais lattices into lattice systems and crystal families is given in the figure 6.6.

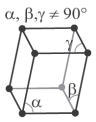
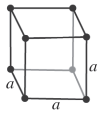
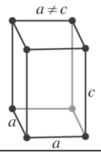
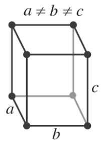
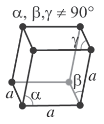
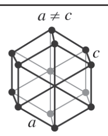
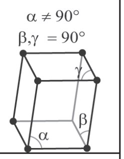
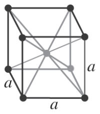
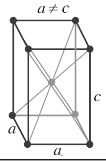
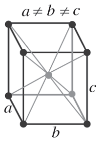
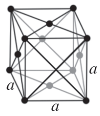
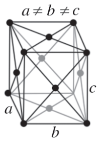
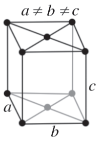
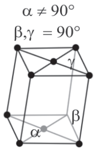
	Triclinic	Cubic	Tetragonal	Orthorobmic	Rhombohedral	Hexagonal	Monoclinic
P							
I							
F							
C							

Figure 6.6. The Fourteen Bravais lattices.

6.7. Law of Crystallography

There are three laws of crystallography which deal with the interfacial angles and the rational indices.

6.7.1. Law of constancy of interfacial angles

Crystals are bound by surface which is usually planner. These surfaces are called faces and where two faces intersect an edge is formed. The angle between the normals to the two intersecting faces is the interfacial angle or the angle between any two faces is called interfacial angle. Although the size of the faces or even shapes of crystals of one and the same substances may vary widely with the condition of formation or other factors, yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout. This is shown in fig 6.7. Now it is clear that although the external shape is different yet the interfacial angles are the same.

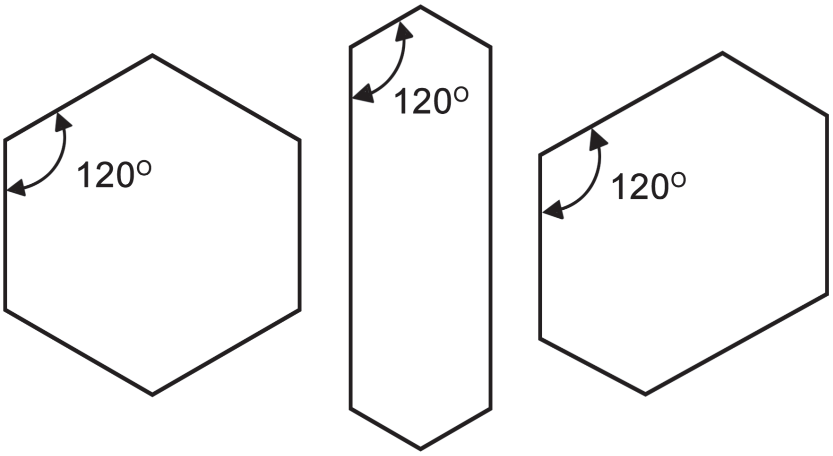


Figure 6.7. Constancy of interfacial angles.

6.7.2. Law of symmetry

The law of symmetry states that, all crystals of the same substance possess the same elements of symmetry. Symmetry in crystals may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal which was described earlier.

6.7.3. Law of rational indices

This law states that the intercepts of any face of a crystal along the crystallographic axes are either equal to the unit intercepts (a, b, c) or some simple whole number multiples of them, e.g., na, n'b, n"c, etc., where n, n', n", etc., are simple whole numbers.

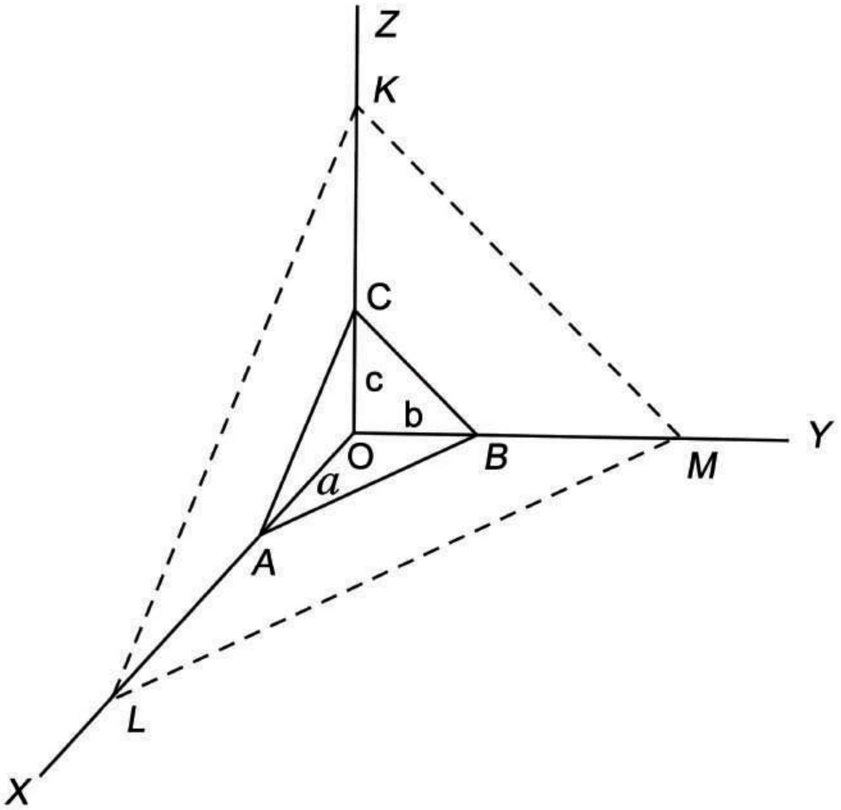


Figure 6.8. Crystallographic axes and the law of rational indices.

Let OX, OY and OZ represent the three crystallographic axes and let ABC be a unit plane (figure 6.8). The unit intercepts will then be a, b and c. According to the above law, the intercepts of any face such as KLM, on the same three axes will be simple whole number multiples of a, b and c, respectively. As can be seen from the figure, the simple multiples in this case are 2, 2 and 3.

6.8. Miller indices

Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axes. The procedure for determination of Miller indices for a plane is as follows:

(i) Write the intercepts as multiples of a, b, c say la, mb, nc

(ii) Take the reciprocals of l, m and n

(iii) Clear fraction to get whole numbers h,k,l.

(iv) Miller indices to the plane are (h,k,l).

Example: calculate the Miller indices of crystal planes which cut through the crystal axes at (i) 2a, 3b, c and (ii) 6a, 3b, 3c

Solutions:

(i)

a	b	c	
2	3	1	intercepts
½	1/3	1	reciprocals
3	2	6	clear fraction

Hence Miller indices are (326)

(ii)

a	b	c	
6	3	3	intercepts
1/6	1/3	1/3	reciprocals
1	2	2	clear fraction

Hence Miller indices are (122)

In a crystal, several planes can be imagined through the lattice points and they are designated by Miller indices. If the Miller indices of a plane is (h, k, l), then all the planes parallel to this plane will have the same Miller indices. The interplanar distance between these parallel planes (d_{hkl}) is given by the following equation:

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

Where h, k, l are the Miller indices of the planes and a, b, c are the dimensions of the cell.

For a cubic system, a = b = c so the distance between two planes (d_{hkl}) in a cubic system

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

6.9. X-Ray diffraction by crystals and Bragg's law

M. von Laue, a German physicist in 1913, suggested the possibility of diffraction of X-rays by crystals as the wavelength of the X-rays was of about the same order as the interatomic distances in a crystal. He has been awarded the 1914 Physics Nobel Prize for his discovery of diffraction of X-rays by crystals. In fact W. H. Bragg succeeded in diffracting X-rays from NaCl crystal. This observation has proved to be highly useful in determining structures and dimensions of crystals.

Bragg's pointed that the scattering of x-rays by crystal could be taken to be equivalent to reflection from successive planes of atoms in the crystal. However the reflection of x-rays can take place only at certain angles which are dependent on wavelength of the x-rays and the distance between the planes of the crystal. The fundamental equation which gives a simple relation between the wavelength of x-rays, the interplaner distance in the crystal and the angle of reflection is known as Bragg's equation.

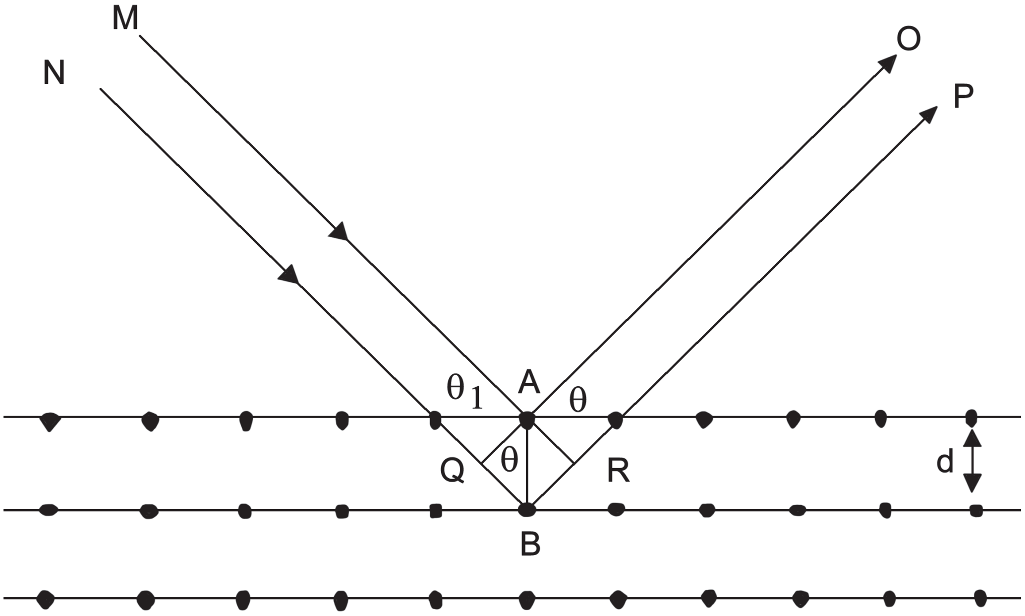


Figure 6.9. X-Ray reflections from a crystal.

The horizontal lines represent parallel planes in the crystal structure separated from one another by a distance d. Suppose, a beam of x-ray (MA) incident at an angle è falls on the crystal and reflected from the crystal (AO). Some of them will be reflected from uppermost plane at the same angle, while the other will be absorbed and get reflected from successive planes, as shown in figure 6.9. Similarly, ray NB is reflected from the second plane to yield BP. If the rays AO and BP are to reinforce one another for constructive interference, they must have the same phase; this condition is met if the extra distance traversed by NBP ray (i.e. QBR) is equal to an integral number of wavelengths of the x-ray. The extra distance is (QB+ BR), so that (QB + BR) = $n\lambda$, where n is an integer. But from the geometry of the situation, QB = BR = d sin θ. Consequently, in terms of the interplanar spacing d, the condition for constructive interference becomes

$$2d \sin \theta = n\lambda, \qquad n = 1, 2, 3, \ldots,$$

which is the fundamental law of x-ray crystallography, the Bragg condition, or Bragg's law. For a given wavelength of x-rays, the reflected beam will emerge only at those angles for which the Bragg condition is satisfied.

6.10. Structure of NaCl, KCl and CsCl

The ionic crystal of NaCl is shown in Fig 6.10. Each sodium ion is surrounding by six chloride ions and each chloride ions is surrounded by six sodium ions. The maximum intensity of reflection occurs at the glancing angle of 5.9^0, 8.4^0 and 5.2^0 for 100, 110 and 111 planes, respectively for first order reflection. From this x-ray diffraction data it can be shown that the NaCl crystal has a face centred cubic (FCC) lattice structure.

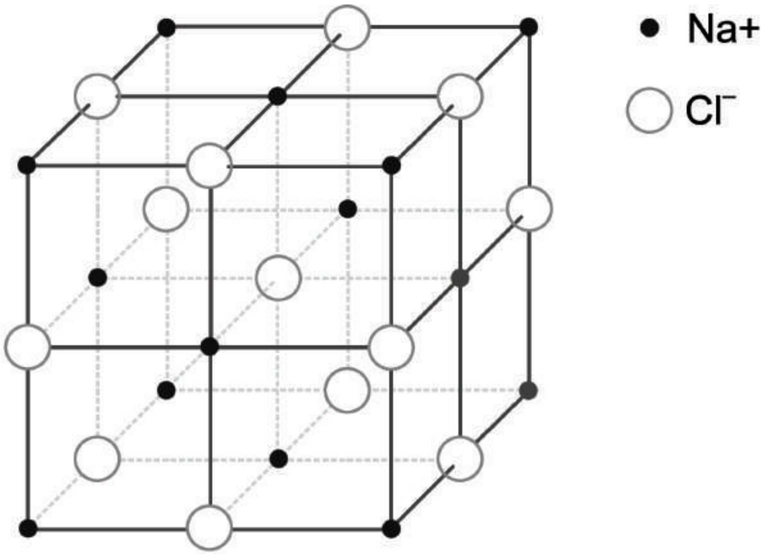


Figure 6.10. Structure of NaCl crystal.

The structure of KCl crystal is similar (isomorphous) to that of NaCl. But investigating the KCl crystal, the maximum reflection of x-rays, corresponding to first order reflections are observed to occur at the glancing angles of 5.38^0, 7.61^0 and 9.38^0 for (100), (110) and (111) faces, respectively which corresponds to a simple cubic lattice structure. The explanation for this apparent anomaly is very simple and can be explained on the basis that the x-rays scattering power for an atom or ion is governed by the number of electrons or atomic number.

The atomic numbers of potassium (K=19) and chlorine (Cl=17) are not very different and the x-rays are unable to detect any difference between the two kinds of atoms. If we imagine all the atoms to be identical, it is evident that face-centred arrangement has become a simple cubic arrangement. This is the reason for the KCl spectrum corresponding apparently to the simple cubic lattice. With KCl, the structure is face-centred, but the face-centred characteristics are marked by the fact that the two types of atoms composing the substance have nearly the same atomic numbers and atomic weights (K=39, Cl=35.5). But in the case of sodium chloride the atomic numbers differ considerably (Na=11, Cl=17), and so their scattering powers are different and hence the true structure as two interpenetrating face-centred lattices become apparent.

Cesium chloride, CsCl, has a body centred cubic (BCC) structure. In its crystal lattice, each Cs^+ ion is surrounded by 8 Cl^- ions and its coordination number is 8. The value of distance between Cs^+ ion and Cl^- ion as determined by Bragg's spectrometer is 3.510Å (figure 6.11).

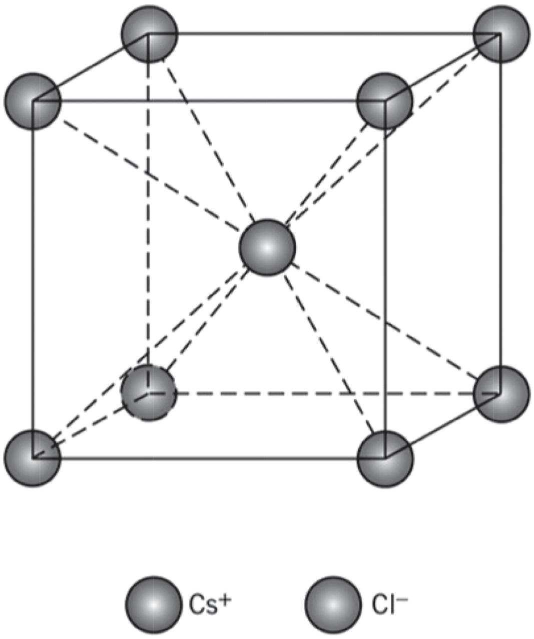


Figure 6.11. Structure of cesium chloride crystal lattice.

6.11. Defects in crystals

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, point defects and line defects. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

Point defects can be classified into three types: (a) stoichiometric defects, (b) impurity defects and (c) non-stoichiometric defects.

(a) **Stoichiometric Defects:** These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically these are of two types, vacancy defects and interstitial defects.

- **(i)** **Vacancy Defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 6.12 i). This results in decrease in density of the substance. This defect can also develop when a substance is heated.
- **(ii)** **Interstitial Defect:** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect (Fig. 6.12 ii). This defect increases the density of the substance.

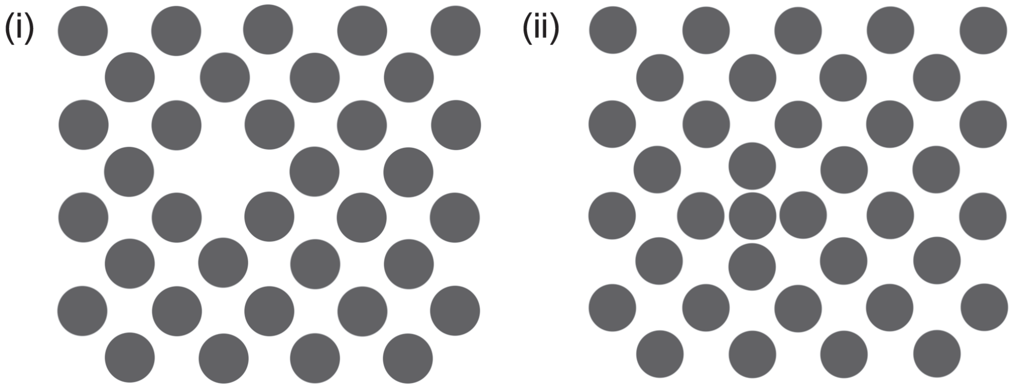
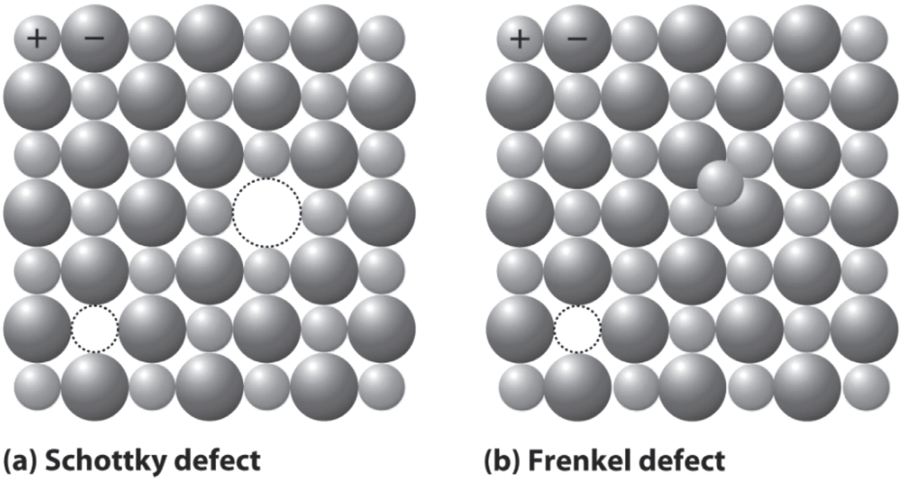


Figure 6.12. Stoichiometric defects: (i) vacancy defect and (ii) interstitial defect.

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Schottky and Frenkel defects.

(iii) Schottky Defect: It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig 6.13a) in the crystal. Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For examples, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.



(a) Schottky defect (b) Frenkel defect

Figure 6.13. Schottky defect and Frenkel defect in a crystal lattice.

(iv) Frenkel Defect: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 6.13b) of the crystal. So it creates a vacancy defect at its original site and an interstitial defect at its new location. Frenkel defect is also called dislocation defect. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

(b) Impurity Defects: If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig 6.14). Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.

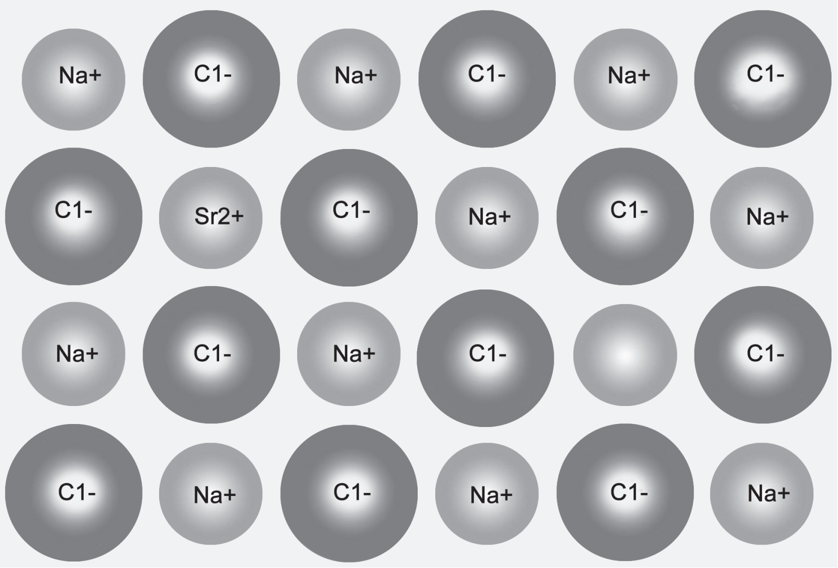


Figure 6.14. Impurity defect in NaCl crystal by presence of Sr^{2+} ion as impurity.

(c) Non-Stoichiometric Defects: The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of nonstoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) **Metal Excess Defect:** This type of defects in crystals can be formed by absence of anion in the lattice site or by the presence of extra cation in the interstitial position.

Metal excess defect due to anionic vacancies: Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig 6.15). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called **F-centres**. They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

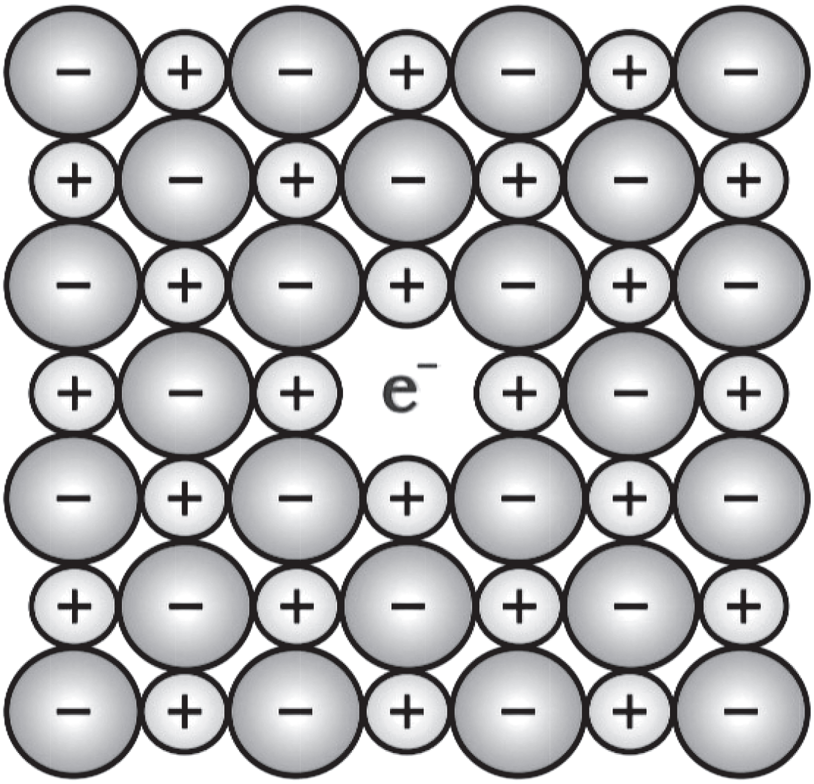


Figure 6.15. Metal excess defect and F-centres.

Metal excess defect due to the presence of extra cations at interstitial sites: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites (Fig 6.16).

(ii) **Metal Deficiency Defect:** There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. In this case some of the metal ions posses' higher valences to maintain the electronutrality of the crystal. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$.

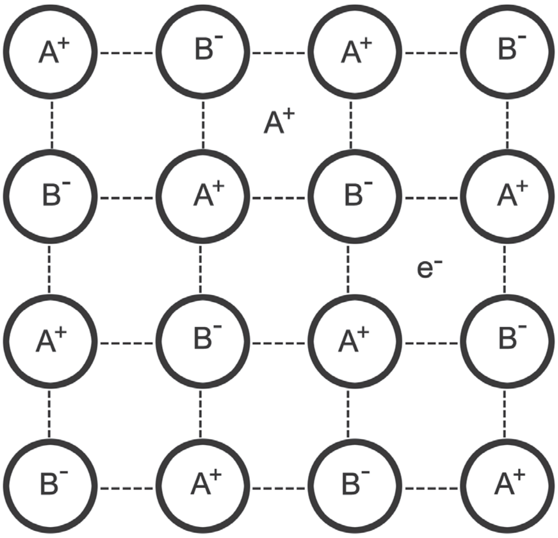


Figure 6.16. Metal excess defect due to the presence of extra cations at interstitial sites.

It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

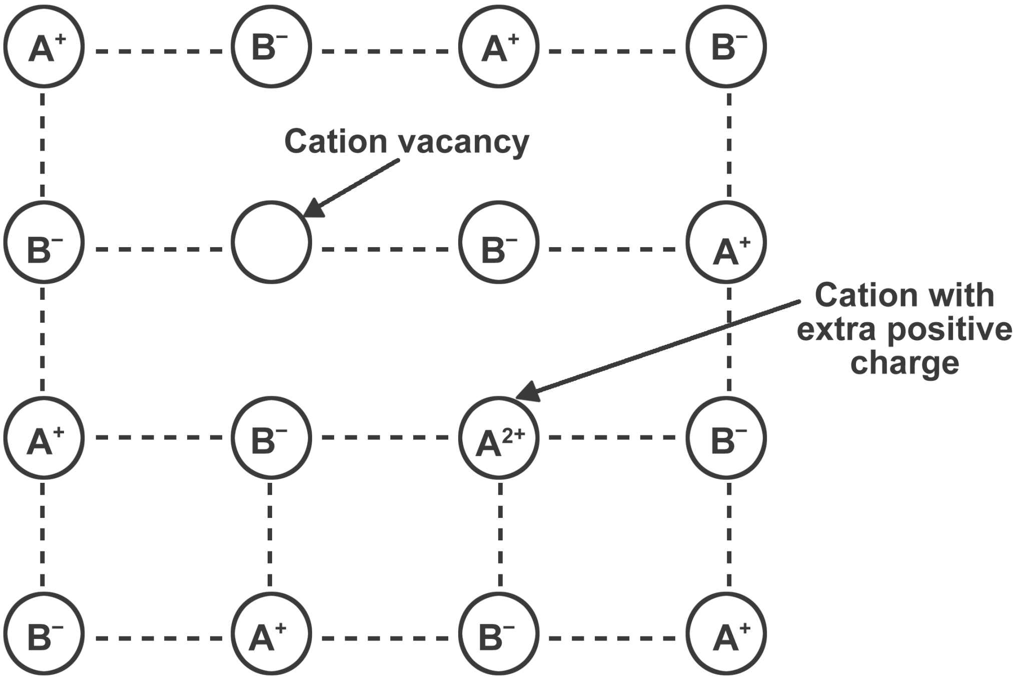


Figure 6.17. Metal deficiency defect in crystals.

6.12. Summary

In this unit, we have briefly described different forms of solid substances and found that they can be distinguished as crystalline and amorphous. We have studied the terms-lattice, basis and unit cell of crystalline solids. Symmetry elements present in the different crystal lattice were discussed. Seven crystal systems and fourteen Bravais lattices were explained. Different laws of crystallography were discussed and indexing of crystal planes was explained. Diffraction method and its utility in crystal structure determination were emphasised on the basis of Bragg's law. Finally different types of crystal defects were highlighted.

6.13. Questions

1. Define the term amorphous. Give a few examples of amorphous solids.
2. What is lattice?
3. Give definition of unit cell.
4. What are the symmetry elements present in a crystal?
5. What is the Miller indices of a crystal plane which makes intercepts 3a/2, 2b, c.? [Ans. (4, 3, 6)]
6. What are the separations of the planes with Miller indices (2, 2, 1) for a cubic lattice of side length 3Å? [Ans. 1 Å]
7. If an X-ray (wavelength = 1.539 Å) gets reflected at an angle of 22.5^0 from a set of crystal planes, then find out the distance between the crystal planes. [Ans. 2.01 Å]
8. Write down the differences in structure between the crystals of NaCl and KCl.
9. What are Frenkel and Schottky defects? Explain with examples.

Unit 7 ❒ Solutions

Contents

7.0. Objectives

After studying this unit, we will be able to

- describe the formation of different types of solutions;
- express concentration of solution in different units;
- state and explain Raoult's law;
- distinguish between ideal and non-ideal solutions;
- explain deviations of real solutions from Raoult's law;

- describe partial miscibility of liquids and critical solution temperature;
- explain steam distillation and solvent extraction process.

7.1. Introduction

Solutions are homogeneous mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as solvent.

Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes. Depending upon the nature of solvent and solute, solutions can be of different types. On the basis of physical state of solute and solvent it can be categorize in the following ways:

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gas (Air)
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

7.2. Units for the Expression of Concentration of Solution

There are several ways by which we can describe the concentration of the solution quantitatively.

Normality: Normality (N) is defined as number of gram equivalent of solute dissolved in one litre (or one cubic decimetre) of solution.

$$\text{Normality} = \frac{\text{Gram equivalent of solute}}{\text{Volume of solution in litre}}$$

For example, 1.00 g.equiv L^{-1} (or 1.00 N) solution of H_2SO_4 means that 1 gram equivalent (49 g) of H_2SO_4 is dissolved in 1 litre of solution.

Molarity: Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

For example, 0.25 mol L^{-1} (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre).

Molality: Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Volume of solvent in kg}}$$

For example, 1.00 mol kg^{-1} (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Mole fraction: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as:

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

For example, in a binary mixture, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B}$$

For a solution containing i number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + n_3 + \dots\dots + n_i} = \frac{n_i}{\sum n_i}$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + x_3 + \dots\dots\dots\dots + x_i = 1$$

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures.

Parts per million (ppm): When a solute is present in trace quantities, it is convenient to express concentration in parts per million (ppm) and it is defined as:

$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Such a small concentration is also expressed as 5.8 g per 10^6 g of sea water or 5.8 ppm. The concentration of pollutants in water or atmosphere is often expressed in terms of μg mL^{-1} or ppm.

7.3. Ideal Solution

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. The ideal solutions have two other important properties. For an ideal solution, enthalpy of mixing is zero ($\Delta H_{mix} = 0$) and volume of mixing is also zero ($\Delta V_{mix} = 0$). It means that no heat is absorbed or evolved when the components are mixed and also final volume of the solution is equal to the sum of volume of two components being mixed. In ideal solution, the interaction between A-B is same as the interaction between A-A and B-B which are the constituent. The partial molar volume of a constituent in an ideal solution is equal to the molar volume of the constituent when present in the pure form. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solutions of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

7.4. Raoult's law

Let us consider a binary solution of two volatile liquids and denote the two components as A and B. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be p_{total} and p_A and p_B be the partial vapour pressures of the two components A and B respectively. These partial pressures are related to the mole fractions x_A and x_B of the two components A and B respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Thus, for component A

$$p_A \propto x_A$$

so, $$p_A = p_A^0 . x_A$$

where p_A^0 is the vapour pressure of pure component A at the same temperature.

Similarly, for component B

$$p_B = p_B^0 . x_B$$

where p_B^0 represents the vapour pressure of the pure component B.

According to Dalton's law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

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

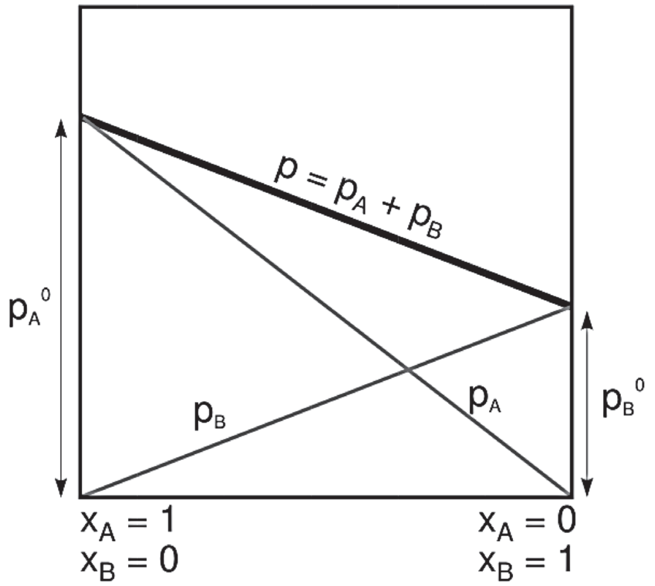


Figure 7.1. The plot of vapour pressure and mole fraction of an ideal solution at constant temperature.

Substituting the values of p_A and p_B, we get

$$p_{total} = x_{A.}p_A^0 + x_B.p_B^0 = (1 - x_B).p_A^0 + x_B.p_B^0 = p_A^0 - x_B\ (p_B^0 - p_A^0)$$

A plot of p_A or p_B versus the mole fractions x_A and x_B for a solution gives a linear plot as shown in Fig. 7.1. These lines (I and II) pass through the points for which x_A and x_B are equal to unity. Similarly the plot (line III) of p_{total} versus x_B is also linear (Fig. 7.1). The minimum value of p_{total} is p_A^0 and the maximum value is p_B^0, assuming that component B is less volatile than component A, i.e., $p_A^0 > p_B^0$.

7.5. Non-ideal Solution and Deviation from Roult's Law

Non- ideal solutions are also known as non- ideal liquid mixtures or real solutions. If a solution does not obey Raoult's law over the entire range of concentration and temperature, the solution is said to be non-ideal solution. The vapour pressures of these solutions are higher or lower than the pressure obtained by using Raoult's law. Here the enthalpy of mixing (ΔH_{mix}) and volume of mixing (ΔV_{mix}) is not equal to zero. In these solutions, the force between A-B is different from A-A and B-B (individual components). Non- ideal solutions are classified into two types: Non- ideal solution showing positive deviation (vapour pressure obtained is higher than calculated using Raoult's law) and non- ideal solution showing negative deviation (vapour pressure obtained is lower than calculated using Raoult's law).

Non-ideal solution showing positive deviation: In the solution of component A and B, the interaction between A-B is weaker than A-A and B-B interaction. In this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. Hence the vapour pressure of the solution is higher than the pressure predicted by Raoult. The enthalpy of mixing is positive. For example, the mixture of ethanol and hexane, acetone and carbon disulphide, carbon tetrachloride and benzene, carbon tetrachloride and toluene shows positive deviation. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution of ethanol and acetone shows positive deviation from Raoult's law. Figure 7.2 represents the curve showing positive deviation.

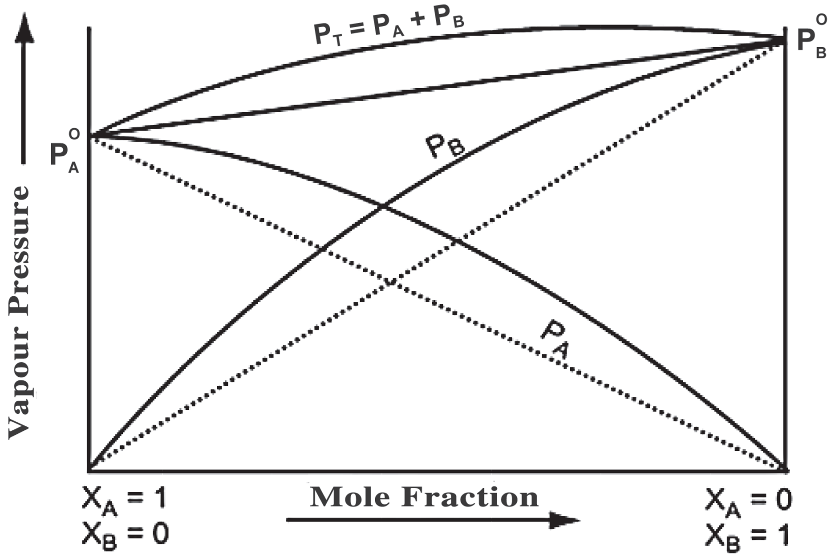


Figure 7.2. The vapour pressures of two component system as a function of composition for a solution that shows positive deviation from Raoult's law.

Non-ideal solution showing negative deviation: In the solution of component A and B, the interaction between A-B is stronger than A-A and B-B interaction. Here the vapour pressure of a solution is lower than the pressure predicted by Raoult. The enthalpy of mixing is negative. For example, the mixtures of acetone and water, phenol and aniline,

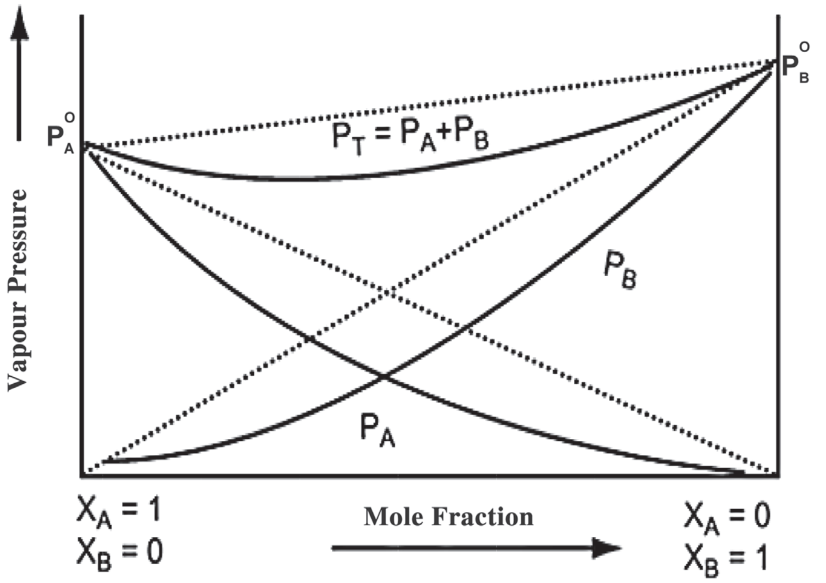


Figure 7.3. The vapour pressures of two component system as a function of composition for a solution that shows negative deviation from Raoult's law.

chloroform and benzene, acetic acid and pyridine shows negative deviation. A mixture of chloroform and acetone shows negative deviation from Raoult's law, because chloroform molecule forms hydrogen bond with acetone molecule which decreases the escaping tendency of molecules for each component. Thus vapour pressure decreases resulting in negative deviation from Raoult's law. Figure 7.3 represents the curve showing negative deviation.

7.6. Vapour Pressure-composition Curves of Ideal and Non-ideal Solutions

So far we have seen the variation of total vapour pressure with the mole fraction of the either constituent in the liquid. Now, in order to find the variation of total vapour pressure with the mole fraction of either A or B in the vapour we can plot the vapour pressure composition curve shown in figure 7.4. Curve I shows the variation of total vapour pressure with respect to the mole fraction in the liquid phase. Similarly, curve II shows the variation of the total vapour pressure with respect to the mole fraction in the vapour phase. It is expected that the mole fraction of a more volatile component in an ideal solution will be more in the vapour phase than in the liquid phase. So the vapour

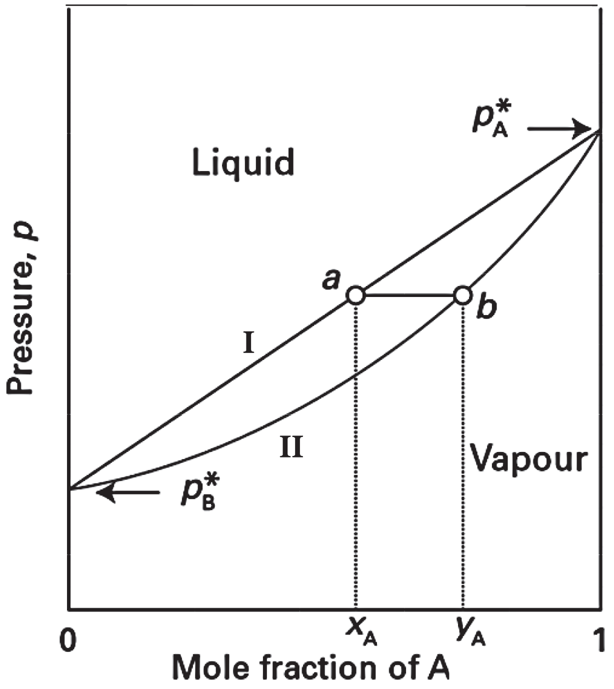


Figure 7.4. Liquid and vapour composition curves for an ideal solution.

phase curve (curve II) lies below the liquid phase curve (curve I). The line ab is called a tie line and it gives us the composition of the solution in the liquid and vapour phases in equilibrium at a particular total vapour pressure.

The curves I and I1 of Fig. 7.4 are obtained in the case of solutions obeying Raoult's law. In the case of solutions showing positive deviation from Raoult's law, the liquid and vapour composition curves are of the type shown in Fig. 7.5. Note that there is a maximum point, M, where both the liquid and vapour phases have the same composition.

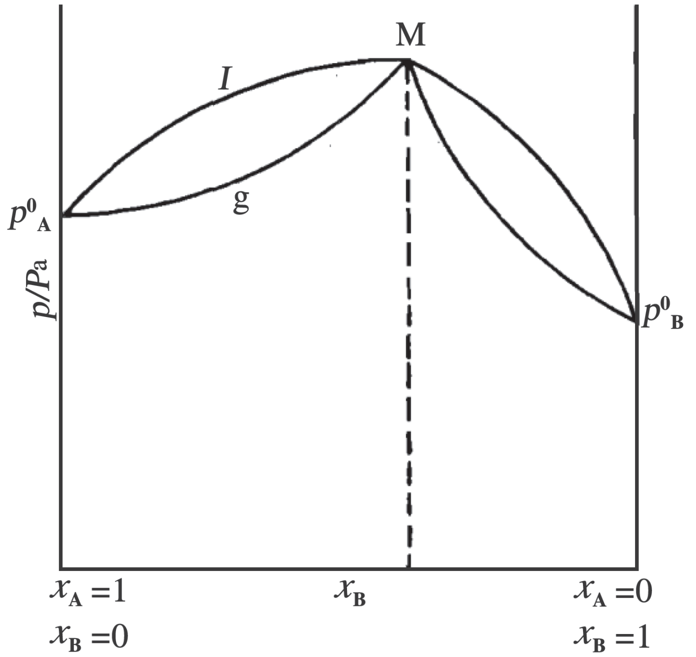


Figure 7.5. Liquid and vapour composition curves for a liquid mixture showing positive deviation.

In the case of a solution showing negative deviation from Raoult's law, the liquid and vapour composition curves are of the type shown in Fig. 7.6. Note that the curves meet at the minimum point M where both the liquid and vapour phases have the same composition.

7.7. Temperature-composition Curves of Ideal and Non-ideal Solutions

Let us consider a binary mixture consisting of two liquids A and B which are completely miscible with each other. On heating under constant pressure, say, under atmospheric

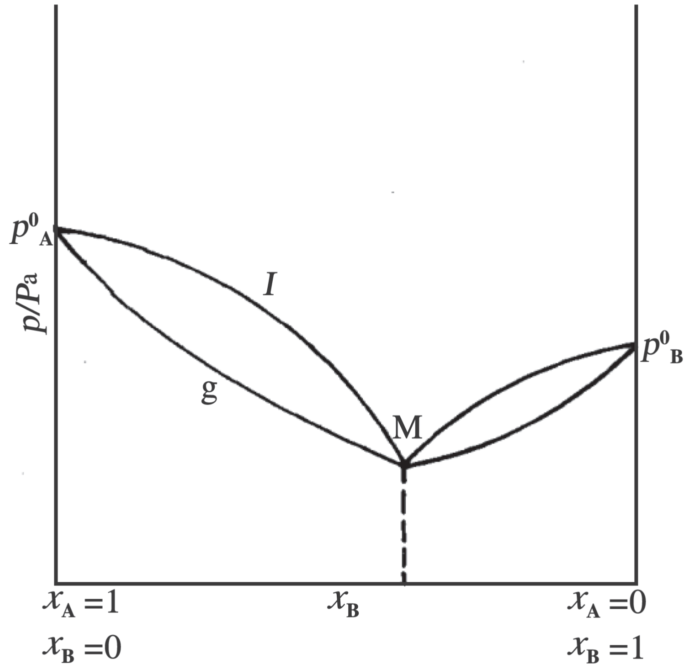


Figure 7.6. Liquid and vapour composition curves for a liquid mixture showing negative deviation.

pressure, it will start boiling when the total vapour pressure becomes equal to the atmospheric pressure. If p represents the atmospheric pressure, then the condition for boiling is

$$p = p_A + p_B$$

where p_A and p_B are the partial pressures of the two components A and B. Since different compositions of a solution have different vapour pressures, the various solutions will not reach a total vapour pressure equal to the atmospheric pressure at the same temperature. Hence, the solutions of different compositions will boil at different temperatures. In general, solutions of low vapour pressure will boil at temperatures higher than those of solutions for which the vapour pressures are high. It is because solutions of high vapour pressure can have the total pressure equal to the atmospheric pressure at relatively lower temperatures as compared to solutions for which vapour pressures are low. Hence it is possible to draw temperature-composition diagrams which will correspond to the three general types of vapour pressure composition diagrams.

For an ideal solution of two miscible liquid A and B the boiling point-composition curve is shown in figure 7.7. Let the vapour pressure of pure A be higher than that of pure B. Consequently at constant pressure, the boiling point of A (T_A) will be lower than that of B (T_B). Now as compared to the liquid mixture, the vapour is richer in the more volatile component. So as in the present case A is more volatile than B, hence, the vapour composition at any temperature must lie closer to A than the corresponding liquid composition. In other words, in the composition against temperature plot, the vapour composition curve must lie above the liquid composition curve. From this plot it can be understood that by boiling the solution from a mixture of two miscible liquids pure liquids can be separated. This process is known as fractional distillation.

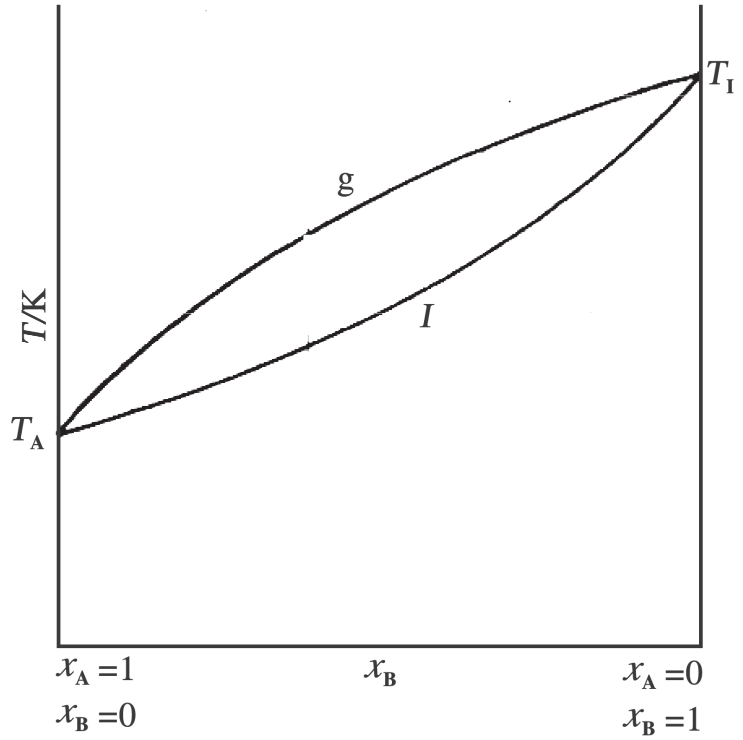


Figure 7.7. Boiling point-composition diagram of an ideal liquid.

Boiling point-composition diagram of a liquid mixture showing positive deviation from Raoult's law is shown in Fig. 7.8(I). Note that this system has a minimum point (C) where the liquid and vapour phases have the same composition. Similarly the boiling point-composition diagram of a liquid mixture showing negative deviation from Raoult's law and it is shown in Fig. 7.8(II). For this type of solutions a maximum point D is observed where the liquid and vapour phases have the same composition.

The constant boiling mixtures having composition C in type I solutions (Fig. 7.8.(I)) and composition D in type II solutions (Fig. 7.8.(II)) are called azeotropes (i.e., liquids boiling unchanged). They resemble pure compounds in their boiling behaviour. However, changes in pressure produce changes in the composition as well as the boiling point of the azeotropes. The azeotropes are not chemical compounds but are rather mixtures resulting from the interplay of intermolecular forces in solution.

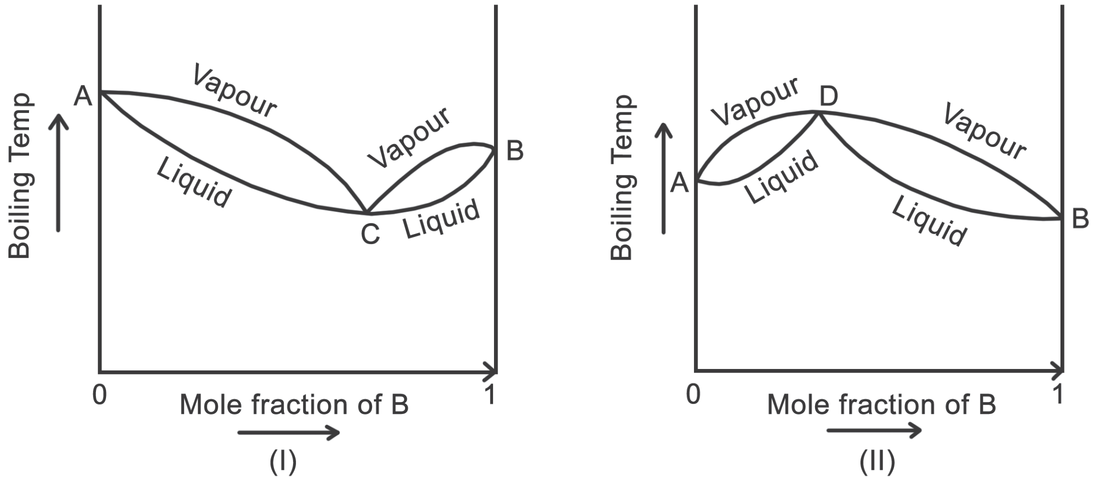


Figure 7.8. (I) Boiling point-composition diagram of a liquid mixture showing positive deviation; (II) Boiling point-composition diagram of a liquid mixture showing negative deviation.

7.8. Partial miscibility of liquids

Some liquid pairs do not form solutions in all compositions. Such liquid pairs are said to be partially miscible liquids. However, due to increased solubility with increase or decrease of temperature, these may become completely miscible.

We can understand such a system by using the example of a system containing phenol and water. When a very small amount of phenol is added to water at room temperature, it dissolves completely to give a single liquid phase. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve anymore. At this point, two phases, i.e., two liquid layers are formed–one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water–rich layer to phenol–rich layer. If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking equal volumes of phenol and water, two layers are formed–one of saturated solution phenol in water and the other of saturated solution water in phenol.

7.9. Critical solution temperature

The temperature above (or below) which a pair of partially miscible liquids becomes miscible in all proportions, is called critical solution temperature (CST) or consolute temperature for the pair.

As discussed earlier, phenol and water are only partially miscible at ordinary temperature. On shaking these two liquids with each other, two saturated solutions of different compositions, one of phenol in water and the other of water in phenol, are obtained. Such solutions of different compositions co-existing with one another are termed conjugate solutions. Since the mutual solubility of phenol and water increases with rise in temperature, the critical solution temperature (CST) lies on top of the dome. Hence, such liquid systems are said to possess an upper critical solution temperature or upper consolute temperature. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8 K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water. Outside the curve we have a homogeneous solution of phenol and water and inside the curve we have two conjugate solutions L1 (phenol in water) and L2 (water in phenol) in equilibrium with each other (Figure 7.9).

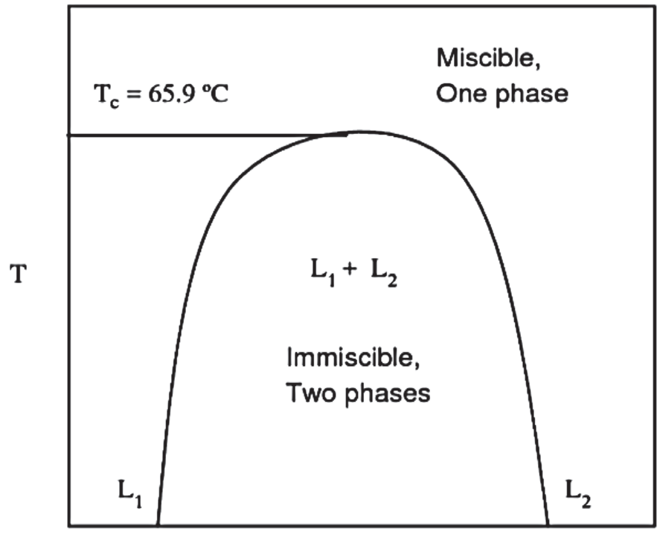


Figure 7.9. Temperature versus solubility plot for phenol-water system.

There are some liquid pairs (e.g., triethylamine-water) for which mutual solubilities decrease with rise in temperature. As the temperature is decreased, the mutual solubilities increase and below the consolute temperature, the two liquids become miscible in all proportions. Such systems possess lower consolute temperature. The variation of mutual solubility of triethylamine and water with temperature is shown in **Fig. 7.10**.

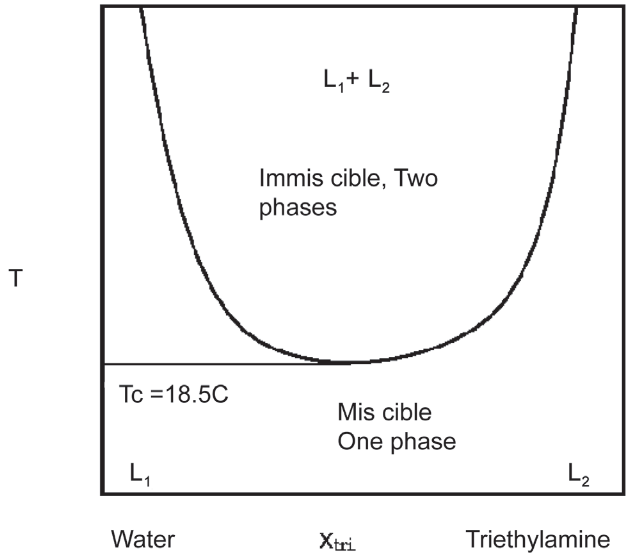


Figure 7.10. Temperature composition diagram for triethylamine-water system.

There are a few liquids pairs, e.g., nicotine and water which show both the upper and lower consolute temperatures. These liquid pairs are completely miscible above a

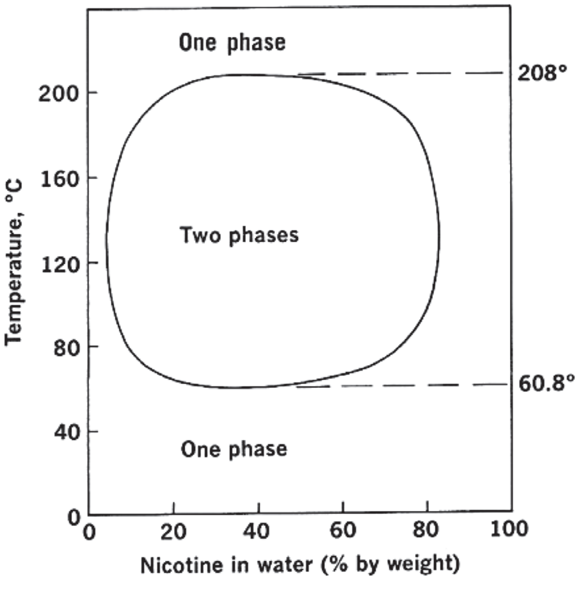


Figure 7.11. Temperature composition diagram for nicotine-water system.

certain temperature (upper consolute temperature) and also below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 7.11.

The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid composition at CST. Substance soluble in only one of the liquids raises the upper CST and lowers the lower CST.

7.10. Principle of steam distillation

The fact, that a system of immiscible liquids starts boiling at temperatures less than the normal boiling points of both the liquids, is made use of in steam distillation. The steam distillation is a process of purifying organic liquids which have high boiling points and are immiscible with water. For purification by steam distillation, an impure compound

i) must be immiscible in water,

ii) should not decompose at the temperature of steam,

iii) should have a fairly high vapour pressure at 373 K,

iv) should have non-volatile impurities.

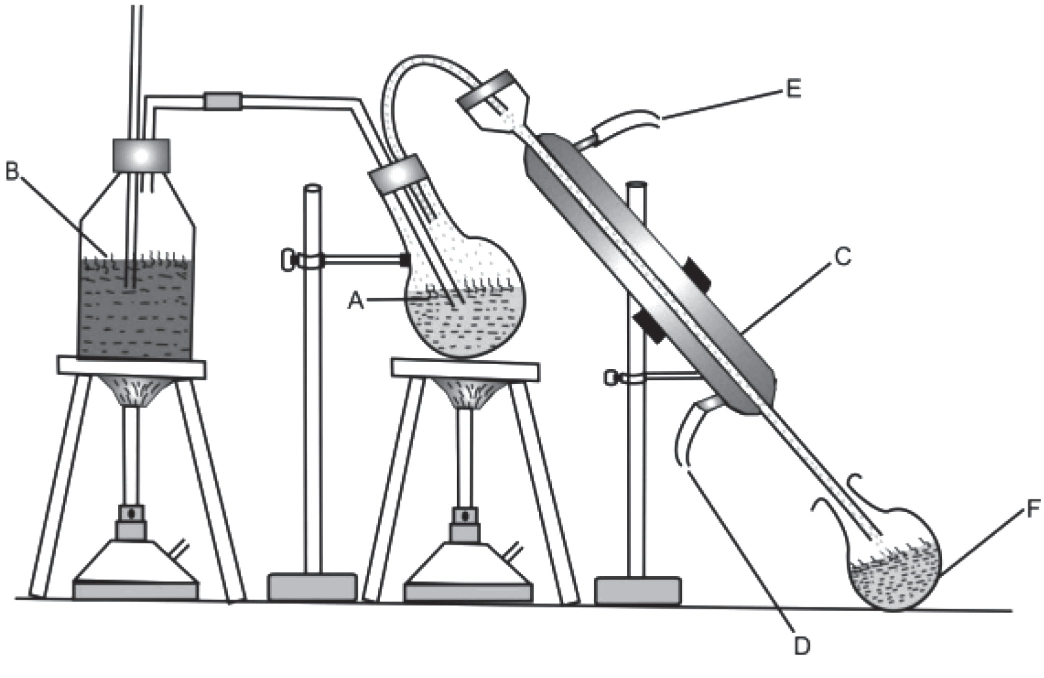


Figure 7.12. Experimental setup for steam distillation.

For example, chlorobenzene has a boiling point of 405 K. A mixture of water and chlorobenzene distils at a constant temperature of 363.3 K, when the external pressure in 9.8×10^4 Pa, by passing steam through it. Let us explain the procedure for purifying an organic liquid using steam distillation. The apparatus used for steam distillation is as shown in Figure 7.12.

The impure organic compound is taken in a round-bottomed flask (A) and a small quantity of water is added. The flask must be kept in a slanting position to prevent the impure liquid from splashing up into the condenser. The flask A is then heated gently. Now, steam from container B is bubbled through the contents of the flask A. Vapours of the organic compound mix with steam and escape into the water condenser C. The condensate thus obtained in the flask F is a mixture of water and the organic compound. This mixture can then be separated by means of a separating funnel.

7.11. Nernst distribution law and its applications

When two immiscible solvents A and B taken in a beaker, they form separate layers. Now a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from B to A. finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = \text{a constant}$$

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents and gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law or Nernst's Partition law or simply Distribution law or Partition law.

It states that,

"if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents."

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed

$$\frac{C_1}{C_2} = K_D$$

The constant K_D (or simply K) is called the distribution coefficient or Partition coefficient or Distribution ratio.

When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, the Distribution Law is also written as,

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

where S_1 and S_2 are the solubilities of the solute in the two solvents.

Limitations of Distribution law:

Nernst distribution law is applicable for the following conditions only

1. Temperature should remain constant
2. Similar molecular species of the solute should remain in the two phases in contact with each other.
3. The solutions should be dilute.
4. The two liquids should be mutually insoluble or only very sparingly soluble (e.g., benzene and water) and their mutual solubility should not be altered by the presence of the solute.

Applications of the Distribution Law:

The study of the distribution of a solute between two immiscible solvents is quite useful in a number of ways. A few of these applications are:

1. Association of the solute molecule in one solvent can be studied from the study of distribution. As for example, by studying the distribution of acetic acid and benzoic acid between water and benzene, it is possible to show that acetic acid and benzoic acid exist as dimers in benzene.

2. If a solute dissociates in one of the solvents, then knowing the distribution coefficient, the degree of dissociation of the solute can be calculated at a particular temperature.
3. The distribution law has also been used in the study of many problems e.g., solvent extraction, analysis and determination of equilibrium constants.

7.12. Solvent extraction

Solvent extraction is used both at laboratory and industrial scale in various processes. An organic compound can often be extracted economically from an aqueous solution or a suspension by,

- adding an organic solvent,
- shaking and separating the two layers, and
- finally, distilling off the organic solvent to recover the separated compound.

In the process of extraction, we make use of the fact that the distribution coefficient of most of the organic compounds is very large in favour of organic solvents. It can be shown that with a given volume of an extracting liquid, the organic compound extracted is more if the given volume of the extracting liquid is used in a number of smaller portions than if the whole of it is used in one portion.

Let us consider an aqueous solution of volume V. Let the mass of an organic compound dissolved in it be w. Let us use volume v of the organic liquid for each extraction and let the mass of the organic compound that remained unextracted in water one extraction be w_1. Then after, the first extraction

Concentration of the organic compound in the aqueous layer = $\frac{w_1}{V}$

Mass of the organic compound in the organic layer = $w - w_1$

Concentration of the organic compound in the organic layer = $\frac{w - w_1}{v}$

Distribution coefficient, K, is given by the following expression:

$$K = \frac{\frac{w_1}{V}}{\frac{w - w_1}{v}} = \frac{w_1 v}{(w - w_1)V}$$

From this expression we get the amount of the organic compound that remained unextracted after first extraction $(w_1) = w\frac{KV}{v+kV}$

Similarly, after the second extraction, the mass of the organic compound that remains unextracted is, $w_2 = w\left(\frac{KV}{v+kV}\right)^2$

In general, the mass of the organic compound that remains unextracted after n extractions is given by, $w_n = w\left(\frac{KV}{v+kV}\right)^n$

7.13. Summary

In this unit we have learnt about the solutions and different type of solutions. Then we have learnt that completely miscible liquid pairs may be ideal or non-ideal. Ideal solutions obey Raoult's law. Non-ideal solutions either show positive or negative deviation from

Raoult's law. We have learnt to draw the vapour pressure-composition and temperature-composition curves for ideal and non-ideal solutions. We have discussed about the partially miscibility of liquids and critical solution temperature. Then we have seen that a pair of immiscible liquids boil at a temperature lower than the boiling points of any of the liquids. This fact is made use of in steam distillation. We have learned about the principle of steam distillation. Finally we have learned about the Nernst distribution law for a system when a solute is added to a pair of immiscible liquids and its applications in solvent extraction.

7.14. Questions

1. Give an example of a solid solution in which the solute is a gas.
2. Define the following terms: (i) Mole fraction (ii) Molality (iii) Molarity.
3. Write down the differences between ideal and non-ideal solution.
4. What is meant by positive and negative deviations from Raoult's law?

5. Draw the phase diagram of phenol-water system and explain the plot.
6. Write down the principle of steam distillation.
7. Describe Nernst distribution law and state its limitations.
8. If the solubility of I_2 in water is 0.345 g/L at 30 ^{0}C then what is the solubility of I_2 in CCl_4 at 30 ^{0}C? Given that the distribution coefficient for I_2 in CCl_4 and water is 86. (Ans. 29.67 g/L)

Unit 8 ❒ Chemical Kinetics

Contents

8.0. Objectives

After studying this unit, we should be able to:

- define rate law, rate constant of reaction,
- discuss the dependence of rate of reactions on pressure, temperature and catalyst

- differentiate between order and molecularity of a reaction,
- state the experimental methods for studying the reaction rates,
- derive integrated rate laws for zero order, first order and second order reactions and use them for calculating rate constants,
- state the methods for determining the order of reaction,
- explain Arrhenius equation and activation energy,
- describe collision theory and activated complex theory.

8.1. Introduction

The branch of physical chemistry which deals with the speed or rate at which a reaction occurs is called chemical kinetics. Chemical Kinetics is the study of rate of a reaction under different conditions like different concentrations, pressures, temperatures, catalyst, pH, dielectric constant of the medium, free radical scavengers, neutral salts etc and suggesting a suitable mechanism for the reaction.

Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rates of reactions proceedings under given condition of temperature, pressure and concentration.

The study of chemical kinetics has been highly useful in determining the factors which influence rate of reaction as well as in understanding mechanism of a number of chemical reactions. The experimental data have led to the development of the modern theories of chemical reactivity of molecules.

In this Unit, we shall be dealing with rate of reaction and the factors affecting these. Some elementary ideas about the collision theory and activated complex theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate.

8.2. The concept of reaction rates

The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction

$$A \rightarrow B$$

The concentration of A decreases and that of B increases with time. The rate of a reaction is defined as the change in concentration of any of reactant or product with time.

As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression

$$r = -\frac{dC_A}{dt} \qquad (1)$$

where $-dc_A$ is very small decrease in concentration of A in a very small time interval dt. Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well.

Thus

$$r = \frac{dC_B}{dt} \qquad (2)$$

where dc_B is very small increase in the concentration of product B in a very small time interval of time dt.

Now it is from (1) and (2)

$$r = -\frac{dC_A}{dt} = \frac{dC_B}{dt} \qquad (3)$$

So for a reaction

$A + B \rightarrow M + N$

the rate can be expressed

$$r = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \frac{dC_M}{dt} = \frac{dC_N}{dt} \qquad (4)$$

Now let us consider a reaction

$aA + bB \rightarrow cC + dD$

In this reaction a moles of A reacts with b moles of B to form c moles of C and d moles of D. The rates of such a reaction can be expressed either in terms of decrease in concentration of a reactant per mole or increase in concentration of a product per mole.

Thus we can write as follows:

$$r = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = \frac{1}{c}\frac{dC_C}{dt} = \frac{1}{d}\frac{dC_D}{dt} = kC_A^a C_B^b \qquad (5)$$

Rate Law and the Rate Constant:

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of reaction in terms of concentration of the reactants is known as rate law. It is also called as rate equation or rate expression. The rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, rate of a reaction depends upon the concentration of reactants.

The rate of the reaction

$A \rightarrow$ Products,

is experimentally found to be given by

$$r = -\frac{dC_A}{dt} = kC_A \qquad (6)$$

where k is the rate constant or the velocity constant of the reaction at the given temperature. This form of rate equation is known as the differential rate equation. If concentration of A is unity, i.e., $C_A = 1$, then, evidently, $r = k$. For a general reaction of the type:

$aA + bB + cC \rightarrow$ Products

The rate of the reaction is given by the rate law expression

$$r = kC_A^a C_B^b C_C^c \qquad (7)$$

If $c_A = c_B = c_C = 1$, then $k = r$. Thus, the rate constant of a reaction, in general is defined as the rate of the reaction when the concentration of each reactant is unity.

8.3. Factors affecting reaction rates

There are a number of factors which affect the rate of a reaction, the most important of them are:

(a) Effect of concentration: The rate of a chemical reaction is influenced by the no. of collisions per second between the reacting molecules. On increasing the concentration of the reactant, the number of collisions will increase and the rate of reaction will increase and on decreasing the concentration the rate will decrease.

(b) Effect of nature of reactants: Reactions between polar or ionic molecules occur almost instantaneously. Those reactions in which the bonds are arranged or electrons are transferred takes a comparatively longer time than the reaction between ionic molecules. We can cite the examples of neutralisation reactions or double displacement reactions which are very fast while the oxidation reduction reactions are slower.

(c) Effect of catalyst: A catalyst can increase or decrease the rate of a chemical reaction. For example the combination of hydrogen and oxygen to form water is slow at ordinary temperature, while it proceeds rapidly in presence of platinum.

(d) Effect of surface area of reactant: Surface area of reactants is of importance only for heterogeneous reactions. With the decrease in the particle size, surface area of the reactant for the same mass increases. The smaller particle thus reacts more rapidly than the larger particles. For example, burning of coal dust in air takes place more rapidly than large lump of coal.

(e) Effect of temperature: With the exception of few reactions, it has been found that generally an increase of temperature increases the rate of reaction. The ratio of rate constants of a reaction at two temperatures differing by 10^0C is known as temperature coefficient of the reaction. The temperatures usually selected for this purpose are 25^0C and 35^0C. Thus

$$\text{Temperature coefficient} = \frac{\text{Rate at } 35^0\text{C}}{\text{Rate at } 25^0\text{C}} = \frac{k_{35}}{k_{25}}$$

The value of temperature coefficient for most of the reactants is close to 2 and in some cases it approaches to 3.

8.4. Order and molecularity of a reaction

In the rate equation (7)

$$r = kC_A^a C_B^b C_C^c$$

a, b and c indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., a + b + c gives the overall order of a reaction whereas a, b and c represent the order with respect to the reactants A, B and C respectively.

Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions.

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved as for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \rightarrow H_2 + I_2$$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$$2NO + O_2 \rightarrow 2NO_2$$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.

It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.

The molecularity of any process can only be small position integers, while order of reaction can have zero as well as fractional values.

8.5. Derivation of integrated rate equations

We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate. This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant. The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations for zero, first and second order chemical reactions.

8.5.1. Zero order reaction

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$A \rightarrow P$$

$$\text{Rate} = r = -\frac{dC_A}{dt} = kC_A^0 \qquad (8)$$

As any quantity raised to power zero is unity

$$-\frac{dC_A}{dt} = kC_A^0 = k \times 1 = k$$

$$dc_A = -k\,dt$$

Let the initial concentration at initial time of the reaction, t= 0 be c_0. Subsequently at any other time t, the concentration will be 'c'. On integration we obtain

$$\int_{c_0}^{c} dc_A = \int_0^t -k\,dt$$

$$c - c_0 = -kt$$

$$c = -kt + c_0 \qquad (9)$$

This is the integrated rate equation for zero order reaction. If we plot concentration (c) against t, we get a straight line (Fig. 8.1) with slope = $-k$ and intercept equal to c_0.

Further simplifying equation (9), we get the rate constant, *k* as

$$k = \frac{c_0 - c}{t} \tag{10}$$

Photochemical reaction between H_2 and Cl_2 over water (saturated with HCl) surface is an example of zero order reaction.

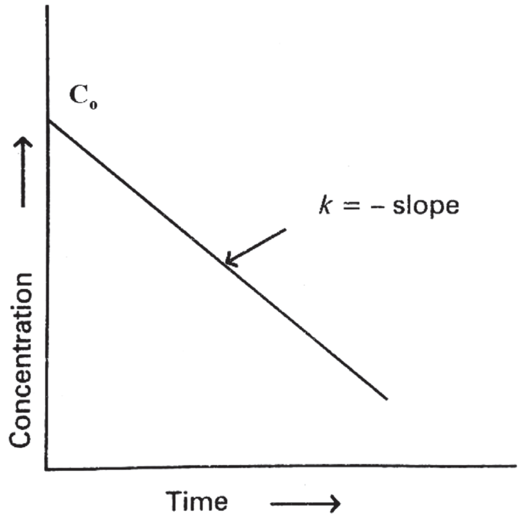


Figure 8.1. Variation in the concentration vs time plot for a zero order reaction.

8.5.2. First order reaction

The differential rate expression for the first-order reaction A → P is given by

$$\text{Rate} = r = -\frac{dc_A}{dt} = \frac{dc_P}{dt} = kC_A$$

Bringing concentration terms in one side and the time on the other side, we can write the above equation as

$$-\frac{dc_A}{c_A} = k_1 dt$$

Now if the initial concentration at initial time t=0 be c_{-0}, and at any other time t, the concentration is c then, by integration we get

$$\int_{c_0}^{c} -\frac{dc_A}{c_A} = \int_0^t k_1 dt$$

$$-\ln\frac{c}{c_0} = k_1 t$$

$$c = c_0 e^{-k_1 t} \qquad (11)$$

From equation 11 we can write

$$k_1 = \frac{1}{t}\ln\frac{c_0}{c} \qquad (12)$$

or, $$k_1 = \frac{2.303}{t}\log\frac{c_0}{c} \qquad (13)$$

This is the expression for the first order rate constant k_1.

Sometimes equation 12 is expressed in another format. If initial concentration of the reactant is a and x moles of it react in time t; then the concentration of the reactant left behind at time t will be a-x. In such a case the equation 12 can be written as

$$k_1 = \frac{1}{t}\ln\frac{a}{a-x} \qquad (14)$$

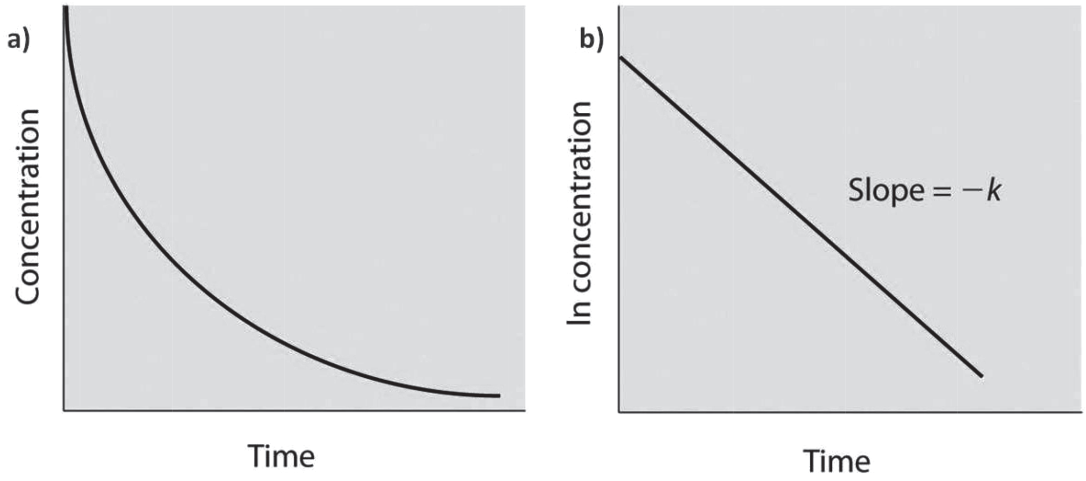


Figure 8.2. The plot of concentration versus time (a) and ln(concentration) versus time (b) for a first-order reaction.

From equation 14 it can be seen that the concentration of reactant in a first order reaction decreases exponentially with time. A plot of ln(concentration) versus time will give a straight line with slope = $-k_1$. This is shown in figure 8.2.

8.5.3. Second order reaction

There are two types of second order reactions

Case I: When both the reactants are same. This, in effect, means that two molecules of the same reactant are involved in the chemical reaction. The second-order reaction in this case would be represented as

$$2A \rightarrow P$$

The rate of the reaction can be expressed as

$$\text{Rate} = r = -\frac{dc_A}{dt} = \frac{dc_P}{dt} = k_2 C_A^2$$

Where k_2 is the second order rate constant. Now if a is the initial concentration of A, x is the concentration of the product formed after time t and (a-x) is the concentration of A remaining at time t, then,

$$\text{Rate} = r = \frac{dx}{dt} = k_2 (a-x)^2 \tag{15}$$

By separating the variables and integrating, we get

$$\int_0^x \frac{dx}{(a-x)^2} = \int_0^t k_2 dt$$

$$\frac{1}{(a-x)} - \frac{1}{a} = k_2 t$$

$$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \tag{16}$$

This is the integrated expression for the rate constant of a second order reaction in which two molecules of the same reactant are involved in the reaction. The most common example of the above type of the second order reaction is the gaseous decomposition of hydrogen iodide.

$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g)$

The rate expression for this reaction is

$$\text{Rate} = r = \frac{d[HI]}{dt} = k_2[HI]^2$$

Case II: When the reactants are different

Consider a second order reaction

$A + B \rightarrow P$

where the initial concentration of A is a mol dm^{-3} and that of B is b mol dm^{-3}. After time t, x mol dm^{-3} of A and x mol dm^{-3} of B react to form x mol dm^{-3} of the product. Thus the reactant concentration at time t are (a–x) and (b–x), respectively. The differential rate expression for the second order reaction is,

$$\text{Rate} = r = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \frac{dc_P}{dt} = k_2C_AC_B$$

This can be written as

$$r = \frac{dx}{dt} = k_2(a-x)\,(b-x) \tag{17}$$

where k_2 is the second order rate constant. Separating the variables, we get

$$\frac{dx}{(a-x)(b-x)} = k_2dt \tag{18}$$

Resolving into partial fractions (assuming that a>b), we can write

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)}\left[\frac{1}{b-x} - \frac{1}{a-x}\right] \tag{19}$$

Using equation 19 in equation 18 and integrating we can write

$$\int_0^x \frac{dx}{(a-x)(b-x)} = \frac{1}{(a-b)}\left[\int_0^x \frac{1}{b-x} - \int_0^x \frac{1}{a-x}\right] = k_2\int_0^t dt \tag{20}$$

By solving this integration we get

$$\frac{1}{(a-b)}\ln\left(\frac{a-x}{b-x}\right)-\frac{1}{(a-b)}\ln\left(\frac{a}{b}\right)=k_2t \qquad (21)$$

Rearranging and solving this equation 21, we get

$$k_2=\frac{1}{(a-b)t}\left[\ln\left(\frac{a-x}{b-x}\right)-\ln\frac{a}{b}\right]=\frac{1}{(a-b)t}\left[\ln\frac{b(b-x)}{a(b-x)}\right] \qquad (22)$$

This is the integrated expression for the rate constant of a second order reaction. Here we have assumed that a > b. If we had assumed b > a then the expression becomes as follows

$$k_2=\frac{1}{(a-b)t}\left[\ln\frac{a(b-x)}{b(a-x)}\right]$$

8.6. Half-life of a Reaction

The time required for a reaction to reduce the concentration of the reactant to the half of its initial concentration is called half life period ($t_{1/2}$).

Half life for a zero order reaction:

For a zero order reaction, from the integrated rate law we get

$$k=\frac{c_0-c}{t}$$

At $t=t_{1/2}, c=\frac{c_0}{2}$

Then, $$t_{\frac{1}{2}}=\frac{c_0-\frac{c_0}{2}}{k}=\frac{c_0}{2k} \qquad (23)$$

So for a zero-order reaction, the half-life period depends on the initial concentration of the reactant and the rate constant.

Half life for a first order reaction:

For the first order reaction

$$k_1 = \frac{2.303}{t}\log\frac{c_0}{c}$$

At $\quad t = t_{1/2},\ c = \frac{c_0}{2}$

$$t_{\frac{1}{2}} = \frac{2.303}{k_1}\log\frac{c_0}{\frac{c_0}{2}}$$

$$t_{\frac{1}{2}} = \frac{2.303}{k_1}\log 2$$

$$t_{\frac{1}{2}} = \frac{0.693}{k_1} \tag{24}$$

It can be seen from equation 24, that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order reaction can be readily calculated from the rate constant and vice versa.

Half life for a second order reaction:

For the second order reaction, we can write from equation 16

$$k_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$

At $\quad x = a/2,\ \ t = t_{1/2}$

$$k_2 = \frac{1}{t_{1/2}}\left[\frac{a/2}{a(a-a/2)}\right] = \frac{1}{t_{1/2}}\frac{a/2}{a\left(\frac{a}{2}\right)} = \frac{1}{a\,t_{1/2}}$$

$$t_{\frac{1}{2}} = \frac{1}{k_2 a} \tag{25}$$

So from equation 25, we can find that $t_{1/2}$ of a second order reaction is inversely proportional to the initial concentration of the reactant and thus it does not remain constant as the reaction proceeds.

Half life for nth order reaction:

It can be shown that for a nth order reaction of

nA → Products

The half life time can be expressed by the following equation

$$t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{k_n (n-1)\, a_0^{n-1}} \tag{26}$$

Where a_0 is the initial concentration of the reactant A and k_n is the nth-order rate constant. From the equation 26 we can see that

$$t_{1/2} \propto \frac{1}{a_0^{n-1}} \tag{27}$$

8.7. General methods for determination of order of a reaction

The order of a reaction is never known before hand, though most of the reactions are of the first or second order. In order to write the rate law, we must know the order of reaction with respect to each reactant. The following methods are commonly used for determining the order of a reaction

i) Method of Initial Rate:

The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction,

A + B → Products

Let the rate of reaction be represented as,

$$r = k\,[A]^m\,[B]^n$$

where the reaction is ***m***th order in A and ***n***th order in B. The rate constant for the reaction is ***k.*** We have to obtain the initial rates from at least two experiments in which the initial concentrations of A (a_1 and a_2) are different while the initial concentration of B (b_1) is constant.

Rate in Experiment **I** = $r_1 = ka_1^m b_1^n$

Rate in Experiment **I1** = $r_2 = ka_2^m b_1^n$

From the ratio $\frac{r_1}{r_2}$, we can calculate order m, since a_1 and a_2 are known

$$\frac{\text{Rate in experiment I}}{\text{Rate in experiment II}} = \frac{r_1}{r_2} = \frac{ka_1^m b_1^n}{ka_2^m b_1^n} = \left(\frac{a_1}{a_2}\right)^m$$

Taking logarithms we can write

$$\log\frac{r_1}{r_2} = m \log\frac{a_1}{a_2} \tag{28}$$

Similarly, the rate for one more experiment in which the initial concentration of A is a_2 and the initial concentration of B is b_2.

So, rate in Experiment **III** = $r_3 = ka_2^m b_2^n$

$$\frac{\text{Rate in experiment II}}{\text{Rate in experiment III}} = \frac{r_2}{r_3} = \frac{ka_2^m b_1^n}{ka_2^m b_2^n} = \left(\frac{b_1}{b_2}\right)^n$$

$$\log\frac{r_2}{r_3} = n \log\frac{b_1}{b_2} \tag{29}$$

Since r_2, r_3, b_1 and b_2 are known, n can be calculated. The overall reaction order = m + n.

ii) Using Integrated Rate Expression:

We can determine the order of reaction

a) by substitution of experimental data into integrated rate law equations; i.e.; in equation 10, 13 and 16.

b) by graphical method using plots such as [A] against t, log[A] against t and 1/[A] against t. The order of the reaction is one, two or zero depending on which of the equations gives rise to a constant value for k or which of the plots gives a straight line.

iii) Half-Life Method:

The half-lives are determined using different initial concentrations of the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the first power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order.

In general, half-life period ($t_{1/2}$) is proportional to $(1/a_0)^{n-1}$ where a_o is the initial concentration of the reactant and *n* is the order of the reaction.

If the half-life periods are $(t_{1/2})_1$ and $(t_{1/2})_2$ corresponding to the initial concentrations a_1 and a_2 of a reactant, then

$$\frac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

or, $$\ln\frac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2} = (n-1)\ln\left(\frac{a_2}{a_1}\right)$$

or, $$n = 1 + \frac{\ln\dfrac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2}}{\ln\left(\dfrac{a_2}{a_1}\right)} \qquad (30)$$

iv) Isolation Method:

In the case of reactions having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. It is equal to the order in the reactant present in lesser quantity. This procedure is repeated in turn with each of the reactants being in lesser amount while others are in excess. This procedure is called van't Hoff s isolation method.

8.8. Concept of activation energy and its calculation from Arrhenius Equation

We have seen about the temperature dependence of rate of a reaction in section 8.3. The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation. Arrhenius proposed the following empirical relationship between the rate constant, k, and temperature, T.

$$k = \mathrm{A}\ \mathrm{e}^{-E\mathrm{a}/RT} \tag{31}$$

where *A* is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. *R* is gas constant and *E*a is activation energy measured in joules/mole (J mol^{-1}).

It can be understood clearly using the following simple reaction

$$H_2\ (g) + I_2\ (g) \rightarrow 2HI\ (g)$$

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

The energy required to form this intermediate, called activated complex (C), is known as activation energy (*E*a). Fig. 8.3 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products. Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

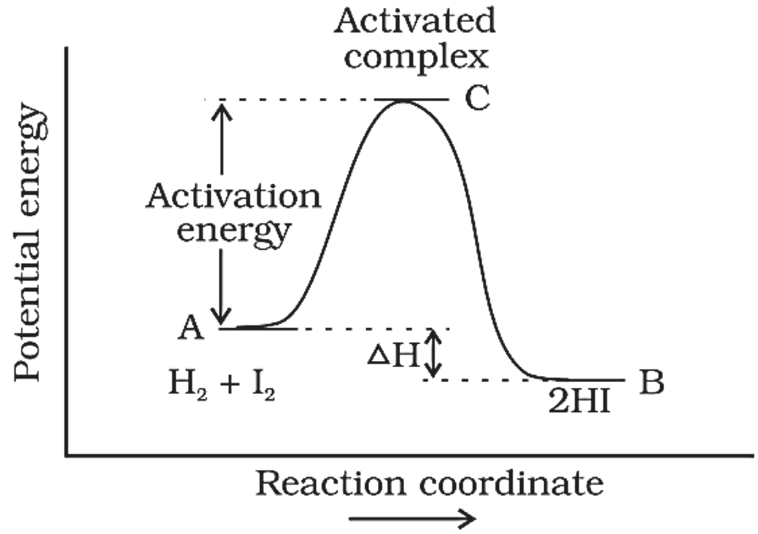


Figure 8.3. Diagram showing plot of potential energy vs. reaction coordinate.

All the molecules in the reacting species do not have the same kinetic energy. For the formation of product the reactant molecules must possess sufficient energy. Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a. Thus, with increase of the reaction temperature the rate of the reaction increases. In the Arrhenius equation (31) the factor $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a.

Taking natural logarithm of both sides of equation 31, we get

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{32}$$

From equation 32, it is evident that a plot of ln*k* versus 1/T (figure 8.4) gives a straight line with slope = – Ea/R and intercept = ln*A*.

By differentiating equation 32 with respect to temperature, we can write

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \tag{33}$$

Integrating equation 33 between temperature T_1 and T_2 when the corresponding rate constants are k_1 and k_2, respectively and assuming that E_a is constant over this temperature range, we obtain

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \tag{34}$$

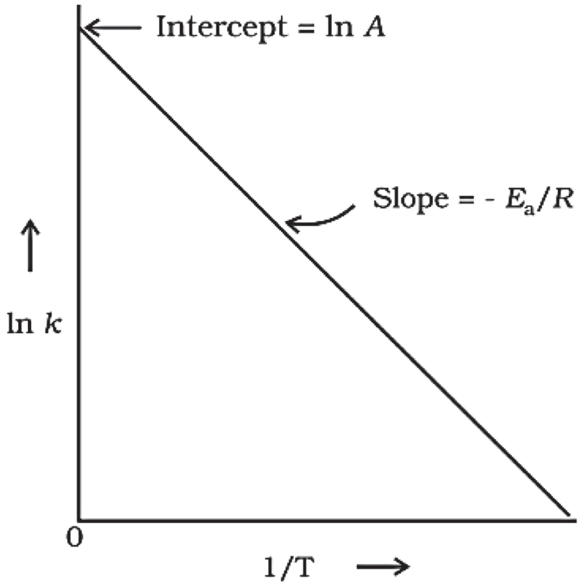


Figure 8.4. Plot of ln k vs 1/T.

This is the integrated Arrhenius equation. From this equation 34 by knowing the rate constants at two different temperatures, the energy of activation E_a can be readily determined.

8.9. Theories of reaction rates

There are two important theories of reaction rates. These are the collision theory developed by Arrhenius and van't Hoff and the modern activated complex theory, or also called the transition state theory developed by Eyring, Polanyi and Evans.

8.9.1. Collision theory

This is the earliest theory of reaction rates. Since reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reactant species must collide before they react. Since our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase, we will restrict our discussion to bimolecular reactions in the gaseous phase.

From the kinetic theory of gases (discussed in unit 4), the number of bimolecular collisions per second per cm^3 among molecules of one species is given by

$$Z = 2n^2\sigma^2\left(\frac{8\pi kT}{M}\right)^{1/2} \tag{35}$$

For a reaction involving two different gases A and B, the rate of bimolecular collisions between unlike molecules is given by

$$Z_{AB} = 2n_A n_B \sigma_{av}^2 \left(\frac{8\pi kT}{\mu}\right)^{1/2} \tag{36}$$

where n_A and n_B are numbers of A and B molecules, respectively, σ_{av} is the average collision diameter defined as $(\sigma_A + \sigma_B)/2$ and μ is the reduced mass defined as $\mu = (m_A m_B)/(m_A + m_B)$. The collision number Z_{AB} is given, in terms of molar masses M_A and M_B of the two gases, by the expression

$$Z_{AB} = n_A n_B \sigma_{av}^2 \left[\frac{(M_A + M_B) 8\pi kT}{M_A M_B}\right]^{1/2} \tag{37}$$

Let us calculate Z_{AB} for the reaction between H_2 and I_2 at 700 K and 1 atm pressure, the quantities of the two gases being 1 mole each. Accordingly, $n_{H_2} = n_{I_2} \approx 10^{19}$ molecules cm^{-3}, $\sigma_{H_2} = 2.2$ Å, $\sigma_{I_2} = 4.6$ Å so that $\sigma_{av} = 3.4$ Å. Hence, according to Eq. 37,

$$Z_{AB} = \left(10^{19}\right)^2 \left(3.4 \times 10^{-8}\right) \left[\frac{(2+254) 8 \times 3.14 \times 8.314 \times 10^7 \times 700}{2 \times 254}\right]^{1/2}$$

$$= 10^{38} \times 1.16 \times 10^{-15} \times 8.58 \times 10^5 \approx 10^{29} \text{ collisions } s^{-1} \text{ cm}^{-3}$$

Since there are approximately 10^{29} collisions per second for 10^{19} molecules of each species, each molecule makes about 10^{10} collisions s^{-1} with the molecules of other species. If each collision were lead to a chemical reaction, then the whole reaction would have been completed in about 10^{-10}s. However this is not in agreement with the experimental value. So each collision does not result in chemical reaction.

In order for a reaction to occur, the energy of collision must equal or exceed the threshold energy. The effective energy is, of course, not the total kinetic energy of the colliding molecules but is, instead, the kinetic energy corresponding to the component at the moment of the relative velocity of the two molecules along the line of their centres at the moment of collision. It is this energy with which the two molecules are pressed together.

The detailed analysis of the dynamics of bimolecular collisions leads to the result that the number of collisions $S^{-1}cm^{-3}$ between molecules A and B, when the relative kinetic energy E along the line of centres is greater than the threshold energy is given by

$$Z'_{AB} = Z_{AB}e^{-E/RT} \tag{38}$$

Assuming that Z'_{AB} gives the rate of relative collisions between A and B, we can write

$$-dn_A/dt = Z'_{AB}$$

$$\text{So,} \quad -dn_A/dt = n_A n_B \sigma_{av}^2 \left[\frac{(M_A + M_B)8\pi kT}{M_A M_B}\right]^{1/2} e^{-E/RT} \text{molecules cm}^{-1}\text{s}^{-1} \tag{39}$$

Now if the concentrations of the reactants are expressed in mol dm^{-3}, then

$$[A] = \frac{10^3 n_A}{n_A} \text{ and } [A] = \frac{10^3 n_B}{N_A} \tag{40}$$

Here NA is Avogadro's number. Hence, the rate law expression

$$-dn_A/dt = k_2[A][B]$$

Can be written as

$$-\frac{10^3 dn_A}{N_A dt} = k_2 \frac{10^6}{(N_A)^2} n_A n_B \tag{41}$$

$$\text{Hence,} \quad k_2 = -\frac{N_A}{10^3 n_A n_B} \times \frac{dn_A}{dt} \tag{42}$$

Using equation 39 for $-dn_A/dt$, we have

$$k_2 = \frac{N_A \sigma_{av}^2}{10^3}\left[\frac{(M_A + M_B)8\pi RT}{M_A M_B}\right]^{1/2} e^{-E/RT} \tag{43}$$

Comparing equation 43 with the Arrhenius equation (Eq 31) $k = \mathrm{A}\ e^{-Ea/RT}$, we find that the Arrhenius pre-exponential factor is given by

$$\mathrm{A} = \frac{\mathrm{N_A}\sigma_{av}^2}{10^3}\left[\frac{(\mathrm{M_A}+\mathrm{M_B})8\pi \mathrm{RT}}{\mathrm{M_A M_B}}\right]^{1/2} \qquad (44)$$

The activation energy E_a, in the Arrhenius equation is thus identified with the relative kinetic energy E along the line of centres of the two colliding molecules which is required to cause a reaction between them.

Now let us calculate A and k_2 for the H_2-I_2 reaction at 700 K, considered in the beginning of this section. E_a has been found to be 167.4 kJ mol^{-1}. Substituting the various values in equation 44, A comes out to be = 6.0 x 1011 dm3 mol-1 s-1. Hence, from Arrhenius equation (Eq 31),

$$k_2 = 6.0 \times 10^{11} dm^3\ mol^{-1}\ s^{-1}.\ \exp(-167400\ J\ mol^{-1}/\ 8.314\ J\ K^{-1}\ mol^{-1}\ .\ 700K)$$

$$= 0.22\ dm^3\ mol^{-1}\ s^{-1}$$

which is comparable with the experimental value of 0.064 $dm^3\ mol^{-1}\ s^{-1}$, considering the uncertainty in the values of the activation energy and average collision diameter.

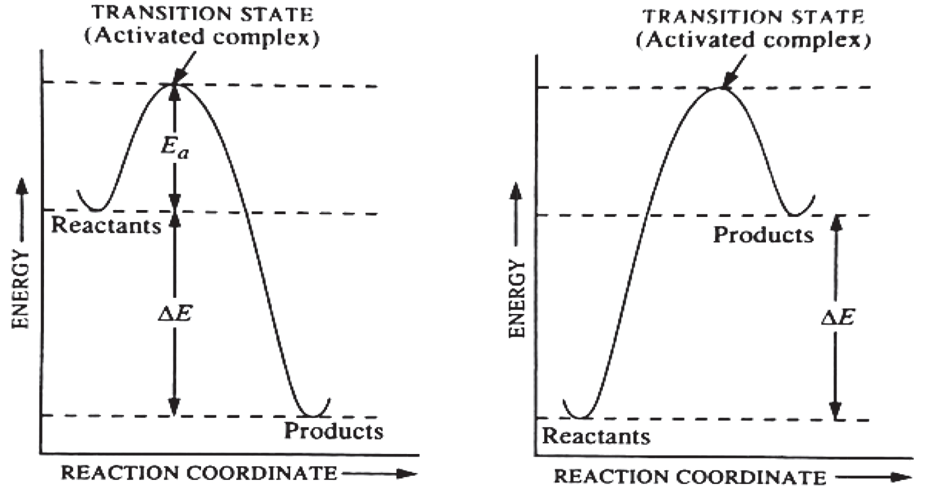
The collision theory is applicable to simple gaseous reactions. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate. The discrepancy arises due to the facts that the colliding reactant molecules are treated as hard spheres without any internal energy. Again the spherical model ignores the dependence of the effectiveness of the collision on the relative orientation of the colliding molecules. Also the activation energy was treated as though it were related entirely on translational motion. For this reasons the collision theory is applicable to reactions between very simple gaseous molecules.

The collision theory can be generalized by introducing the so-called steric factor, p, into the equation for the bimolecular rate constant in order to take account of the orientational requirement. Accordingly the equation becomes

$$k_2 = p\ A\ e^{-Ea/RT} \qquad (45)$$

8.9.2. Activated complex theory of bimolecular reactions

As a result of the development of the quantum mechanics, another theoretical approach to chemical reaction rates has been developed which gives a deeper understanding of the reaction process. It is known as the absolute reaction rate theory or the transition state theory or more commonly as activated complex theory. According to the activated complex theory, the bimolecular reaction between two molecules A_2 and B_2 progresses through the formation of the so-called activated complex which then decomposes to yield the product AB. It must be remembered that the activated complex is not merely an intermediate in the process of breaking or forming of chemical bonds. It is unstable because it is situated at the maximum of the potential energy barrier separating the products from the reactants (Figure 8.5). The difference between the energy of the activated complex and the energy of the reactants is the activation energy, Ea.



(a) Exothermic reaction *(b)* Endothermic reaction

Figure 8.5. Energy versus reaction coordinate in activated complex theory in the case of an exothermic and endothermic reaction.

Let us consider a simple bimolecular reaction

$$A + B \overset{K^\#}{\longleftrightarrow} (AB)^\# \xrightarrow{k_2} \text{Products} \tag{46}$$

where $(AB)^\#$ is the activated complex and $K^\#$ is the equilibrium constant between the reactants and activated complex. From classical mechanics, the energy of vibration of the activated complex $(AB)^\#$ is given by RT/N_A (or k_BT where k_B is the Boltzmann constant) whereas from quantum mechanics, it is given by hv so that $hv = RT/N_A$ or $v = RT/N_Ah = k_BT/h$. The vibrational frequency v is the rate at which the activated complex molecules move across the energy barrier. Thus, the rate constant k_2 can be identified with v.

The reaction rate is given by

$$-\frac{dA}{dt} = \kappa k_2\left[(AB)^{\#}\right] = \kappa\frac{k_BT}{h}\left[(AB)^{\#}\right] \tag{47}$$

where the factor κ, called the transmission coefficient, is a measure of the probability that a molecule, once it passes over the barrier, will keep on going ahead and not return. The value of κ is taken to be unity; it is thus omitted from the rate expression. The concentration of the activated complex $[(AB)^{\#}]$, can be obtained by writing the equilibrium expression

$$K^{\#} = \frac{\left[(AB)^{\#}\right]}{[A][B]}$$

Hence $\left[(AB)^{\#}\right] = K^{\#}[A][B]$ (48)

Substituting the value in equation 47, we get

$$-\frac{dA}{dt} = \frac{k_BT}{h}K^{\#}[A][B] \tag{49}$$

Thus the rate constant k_2 may be expressed as

$$k_2 = \frac{k_BT}{h}K^{\#} \tag{50}$$

The equilibrium constant $K^{\#}$ can be expressed in terms of $(\Delta G^o)^{\#}$, called the standard Gibbs free energy of activation.

Since for the activated complex, we can write

$$\left(\Delta G^0\right)^{\#} = -RT\ln K^{\#} \text{ and } \left(\Delta G^0\right)^{\#} = \left(\Delta H^0\right)^{\#} - T\left(\Delta S^0\right)^{\#} \tag{51}$$

Here, $(\Delta H^o)^{\#}$ is the standard enthalpy of activation and $(\Delta S^o)^{\#}$ is the standard entropy of activation

So we can write, $K^{\#} = e^{-(\Delta G^0)^{\#}/RT} = e^{-(\Delta S^0)^{\#}/R}.e^{-(\Delta H^0)^{\#}/RT}$ (52)

Now substituting in equation 50, we get

$$k_2 = \frac{k_B T}{h} e^{(\Delta S^0)^{\#}/R} . e^{-(\Delta H^0)^{\#}/RT}$$

This is the well known Eyring equation. The application of the activated complex theory is to reactions in solution is quite complicated because of the participation of the solvent molecules in the activated complex. Fortunately, the Eyring equation is applicable for reactions in the solutions phase also.

Taking logs of both sides of equation 53 and differentiating with respect to T we get

$$d\ln k_2/dT = -(\Delta H^0)^{\#}/RT^2 + 1/T = \left[(\Delta H^0)^{\#} + RT\right]\Big/RT^2 \qquad (54)$$

Also, from the Arrhenius equation we get,

$$d\ln k_2/dT = E_a\big/RT^2 \qquad (55)$$

By comparing equation 54 and 55, we obtain

$$E_a = (\Delta H^0)^{\#} + RT$$

or, $$(\Delta H^0)^{\#} = E_a - RT \qquad (56)$$

Again, by comparing equation 53 and 45, we have

$$pAe^{-Ea/RT} = \frac{k_B T}{h} e^{(\Delta S^0)^{\#}/R} . e^{-(\Delta H^0)^{\#}/RT} \qquad (57)$$

If $E_a \approx (\Delta H^0)^{\#}$, wecan equate the exponential factors in equation 57

$$p\,A = \frac{k_B T}{h} e^{(\Delta S^0)^{\#}/R} \qquad (58)$$

For a first order gaseous reaction, p = 1 and A = 10^{10} s^{-1}.

At room temperature the value of $\frac{k_B T}{h} = 10^{13} s^{-1}$.

Hence,

$$e^{(\Delta S^0)^\#/R} = \frac{10^{10}s^{-1}}{10^{13}s^{-1}} = 10^{-3}$$

$$(\Delta S^0)^\# = -57.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

So if $p < 1$ (as in the case of complex molecules) $(\Delta S^o)^\#$ is lower than this value. Qualitatively, a negative value of entropy of activation corresponds to an increase in molecular order in the activated complex relative to the reactant molecules. A large negative value of $(\Delta S^o)^\#$ corresponds to a highly ordered activated complex and this implies a small value of the steric factor. Finally it may be remarked that for reactions involving simple molecules, the collision theory and the activated complex theory give identical results.

8.10. Summary

In this unit, we started with the definitions of the terms such as, rate of reaction, rate law, order and molecularity of reaction. We derived the integrated forms of rate expressions for first order, second order and zeroth order reactions. We have discussed about the half life of the different order reactions. We explained the methods of determination of order of reaction. Finally the concepts of activation energy, Arrhenius equation, collision theory and the activated complex theory were discussed.

8.11. Questions

1. Rate of reaction depends upon which factors?
2. What are the differences between order and molecularity of a reaction?
3. What do you mean by a zero order reaction? Give example.
4. Show that half life of a first order reaction does not depend on the initial concentration of the reactants.
5. Describe any method for determination of order of reaction.
6. How the rate of a reaction depends upon temperature?
7. What is activation energy of a reaction?

8. Why the rate of a reaction increases in the presence of a catalyst?

9. The half life of a first order reaction is 15 min. What is the rate of the reaction? How much time it will take to complete the 80 % of the reaction?

   (Ans. 0.0462 min^{-1}, 34.84 min)

10. The rate of a reaction is 3.46×10^{-5} min^{-1} and 4.87×10^{-5} min^{-1} at 298 K and 338 K respectively. Calculate the activation energy of the reaction. Given the value of $R = 1.987$ cal deg^{-1} mol^{-1}. (Ans. 24.756 kcal/mol)

8.12 Further Readings

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Notes