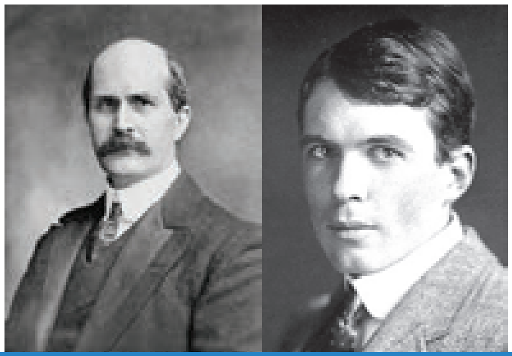
UNIT 6

SOLID STATE



Sir William Henry Bragg (1862 –1942)

Sir Lawrence Bragg (1890 –1971)

Sir William Henry Bragg was a British physicist, chemist, and a mathematician. Sir William Henry Bragg and his son Lawrence Bragg worked on X-rays with much success. They invented the X-ray spectrometer and founded the new science of X-ray crystallography, the analysis of crystal structure using X-ray diffraction. Bragg was joint winner (with his son, Lawrence Bragg) of the Nobel Prize in Physics in 1915, for their services in the "analysis of crystal structure by means of ray". The mineral Braggite (a sulphide ore of platinum, palladium and Nickel) is named after him and his son.

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Learning Objectives

After studying this unit, the students will be able to

- describe general characteristics of solids
- distinguish amorphous and crystalline solids
- define unit cell
- describe different types of voids and close packed structures
- calculate the packing efficiency of different types of cubic unit cell
- solve numerical problems involving unit cell dimensions
- explain point defects in solids

INTRODUCTION

Matter may exist in three different physical states namely solid, liquid and gas. If you look around, you may find mostly solids rather than liquids and gases. Solids differ from liquids and gases by possessing definite volume and definite shape. In the solids the atoms or molecules or ion are tightly held in an ordered arrangement and there are many types of solids such as diamond, metals, plastics etc., and most of the substances that we use in our daily life are in the solid state. We require solids with different properties for various applications. Understanding the relation between the structure of solids and their properties is very much useful in synthesizing new solid materials with different properties.

In this chapter, we study the characteristics of solids, classification, structure and their properties; we also discuss the crystal defects and their significance.

6.1 General characteristics of solids

We have already learnt in XI STD that gas molecules move randomly without exerting reasonable forces on one another. Unlike gases, in solids the atoms , ions or molecules are held together by strong force of attraction. The general characteristics of solids are as follows,

(i) Solids have definite volume and shape.

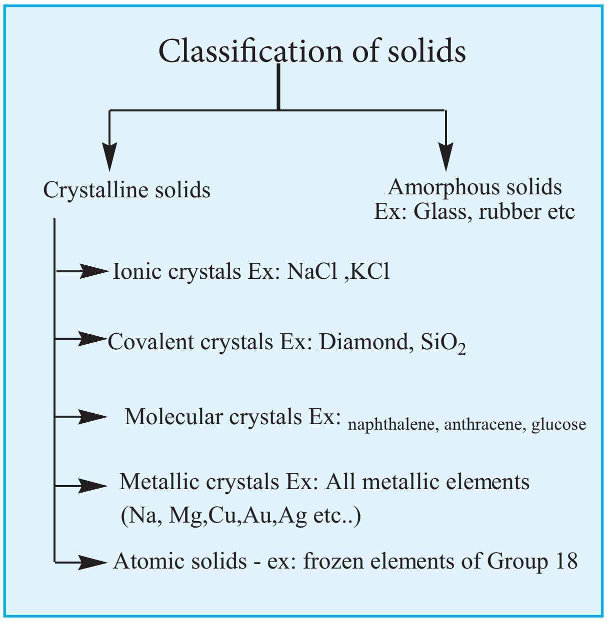
(ii) Solids are rigid and incompressible

(iii) Solids have strong cohesive forces.

(iv) Solids have short inter atomic, ionic or molecular distances.

(v) Their constituents (atoms , ions or molecules) have fixed positions and can only oscillate about their mean positions

6.2 Classification of solids:



We can classify solids into the following two major types based on the arrangement of their constituents.

(i) Crystalline solids

(ii) Amorphous solids.

The term crystal comes from the Greek word “krystallos” which means clear ice. This term was first applied to the transparent quartz stones, and then the name is used for solids bounded by many flat, symmetrically arranged faces.

A crystalline solid is one in which its constituents (atoms, ions or molecules), have an orderly arrangement extending over a long range. The arrangement of such constituents in a crystalline solid is such that the potential energy of the system is at minimum. In contrast, in amorphous solids (In Greek, amorphous means no form) the constituents are randomly arranged.

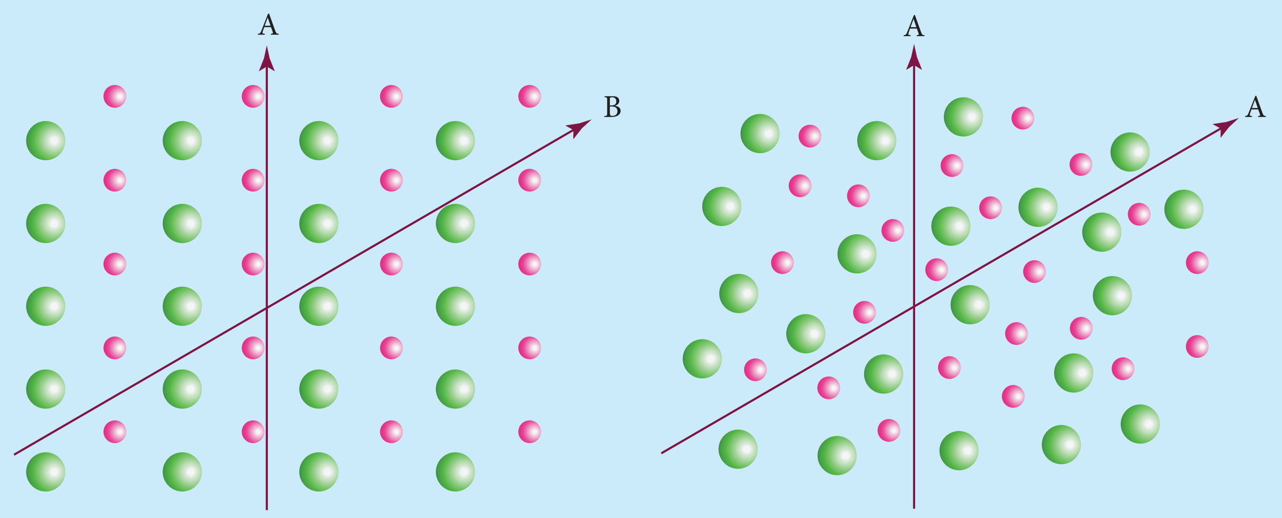
The following table shows the differences between crystalline and amorphous solids.

S.no	Crystalline solids	Amorphous solids
1	Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
2	Definite shape	Irregular shape
3	Generally crystalline solids are anisotropic in nature	They are isotropic* like liquids
4	They are true solids	They are considered as pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded.
7	Examples: NaCl , diamond etc.,	Examples: Rubber , plastics, glass etc

Table 6.1 differences between crystalline and amorphous solids

*Isotropy

Isotropy means uniformity in all directions. In solid state isotropy means having identical values of physical properties such as refractive index, electrical conductance etc., in all directions, whereas anisotropy is the property which depends on the direction of measurement. Crystalline solids are anisotropic and they show different values of physical properties when measured along different directions. The following figure illustrates the anisotropy in crystals due to different arrangement of their constituents along different directions.

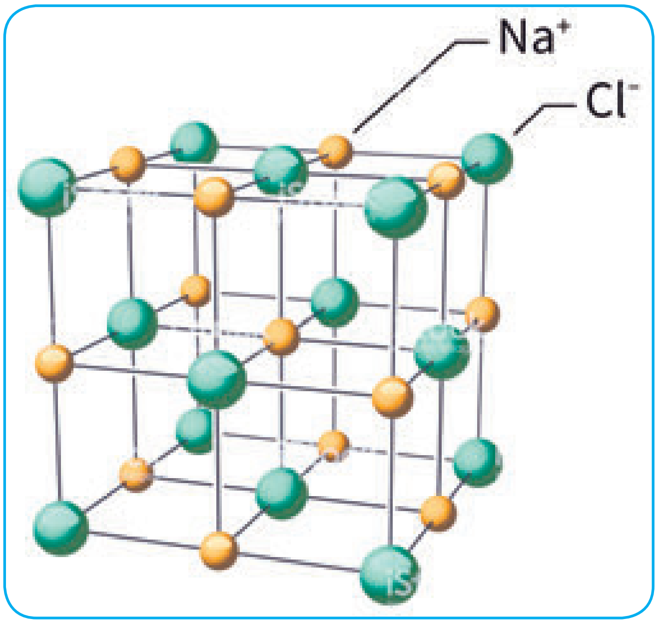


Anisotropy in Crystals **Isotropy in Amorphous solids**

6.3 Classification of crystalline solids:

6.3.1 Ionic solids:

The structural units of an ionic crystal are cations and anions. They are bound together by strong electrostatic attractive forces. To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa. Ionic crystals possess definite crystal structure; many solids are cubic close packed. Example: The arrangement of Na^+ and Cl^- ions in NaCl crystal.



Characteristics:

1. Ionic solids have high melting points.
2. These solids do not conduct electricity, because the ions are fixed in their lattice positions.
3. They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.
4. They are hard as only strong external force can change the relative positions of ions.

6.3.2 Covalent solids:

In covalent solids, the constituents (atoms) are bound together in a three dimensional network entirely by covalent bonds. Examples: Diamond, silicon carbide etc. Such covalent network crystals are very hard, and have high melting point. They are usually poor thermal and electrical conductors.

6.3.3 Molecular solids:

In molecular solids, the constituents are neutral molecules. They are held together by weak van der Waals forces. Generally molecular solids are soft and they do not conduct electricity. These molecular solids are further classified into three types.

DO YOU KNOW?

Graphite is used inside pencils.it slips easily off the pencil onto the paper and leaves a blackmark. Graphite is also a component of many lubricants , for example bicycle chain oil , because it is slippery

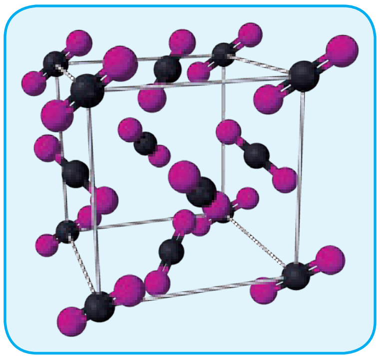
(i) Non-polar molecular solids:

In non polar molecular solids constituent molecules are held together by weak dispersion forces or London forces.

They have low melting points and are usually in liquids or gaseous state at room temperature. Examples: naphthalene, anthracene etc.,

(ii) Polar molecular solids

The constituents are molecules formed by polar covalent bonds. They are held together by relatively strong dipole-dipole interactions. They have higher melting points than the non-polar molecular solids. Examples are solid CO_2 , solid NH_3 etc.



(iii) Hydrogen bonded molecular solids

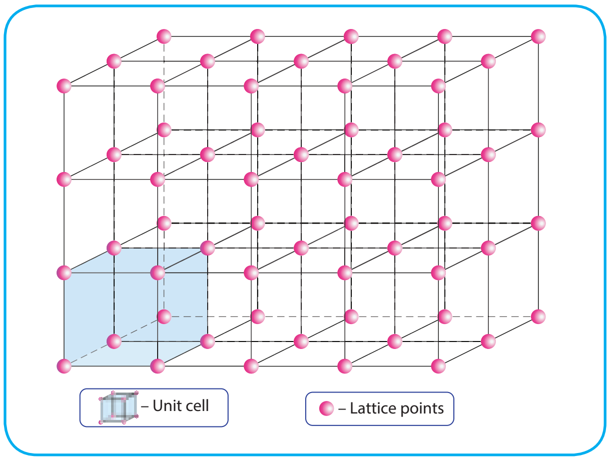
The constituents are held together by hydrogen bonds. They are generally soft solids under room temperature. Examples: solid ice (H_2O), glucose, urea etc.,

6.3.4 Metallic solids:

You have already studied in XI STD about the nature of metallic bonding. In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space. They are hard, and have high melting point. Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre. Examples: Metals and metal alloys belong to this type of solids, for example Cu,Fe,Zn, Ag ,Au, Cu-Zn etc.

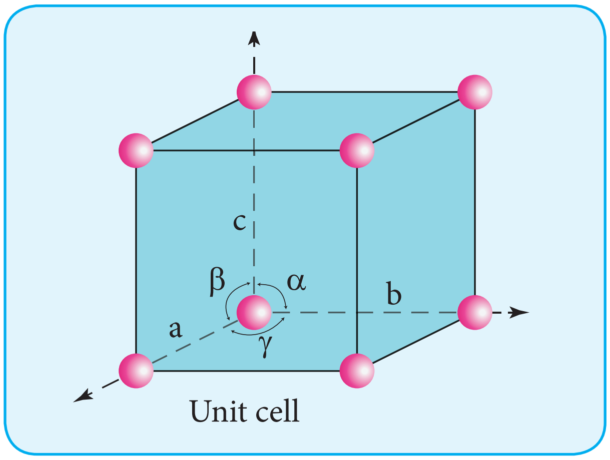
6.4 Crystal lattice and unit cell:

Crystalline solid is characterised by a definite orientation of atoms, ions or molecules, relative to one another in a three dimensional pattern. The regular arrangement of these species throughout the crystal is called a crystal lattice. A basic repeating structural unit of a crystalline solid is called a unit cell. The following figure illustrates the lattice point and the unit cell.



A crystal may be considered to consist of large number of unit cells, each one in direct contact with its nearer neighbour and all similarly oriented in space. The number of nearest neighbours that surrounding a particle in a crystal is called the coordination number of that particle.

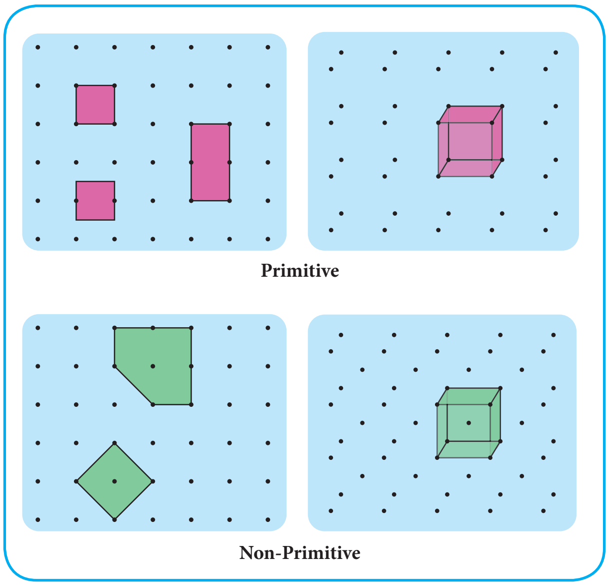
A unit cell is characterised by the three edge lengths or lattice constants a ,b and c and the angle between the edges α, β and γ



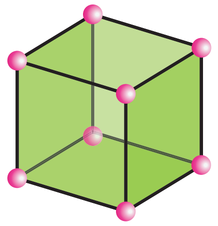
6.5 Primitive and non-primitive unit cell

There are two types of unit cells: primitive and non-primitive. A unit cell that contains only one lattice point is called a primitive unit cell, which is made up from the lattice points at each of the corners.

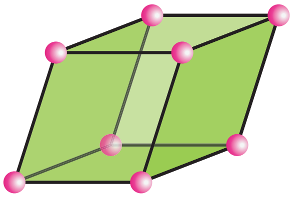
In case of non-primitive unit cells, there are additional lattice points, either on a face of the unit cell or with in the unit cell.



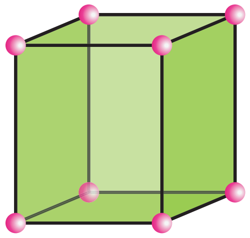
There are seven primitive crystal systems; cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral. They differ in the arrangement of their crystallographic axes and angles. Corresponding to the above seven, Bravis defined 14 possible crystal systems as shown in the figure.



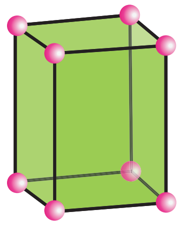
Cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$



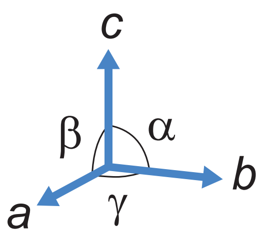
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

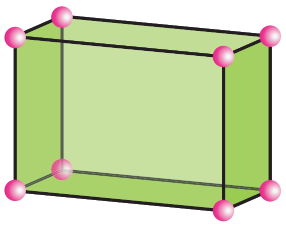


Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

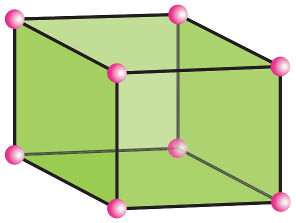


Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

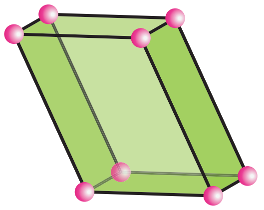




Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

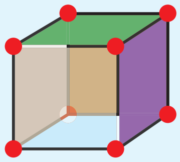
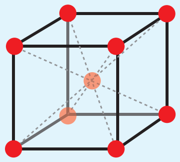
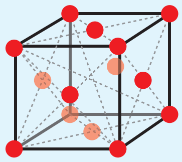
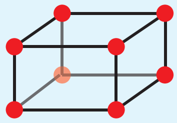
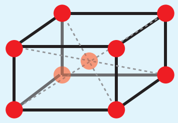
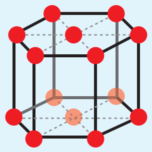
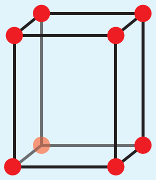
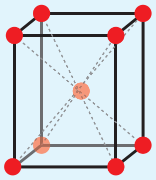
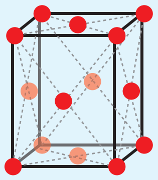
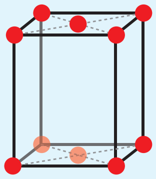
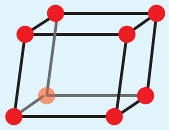
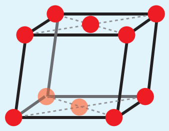
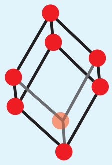
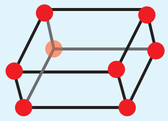
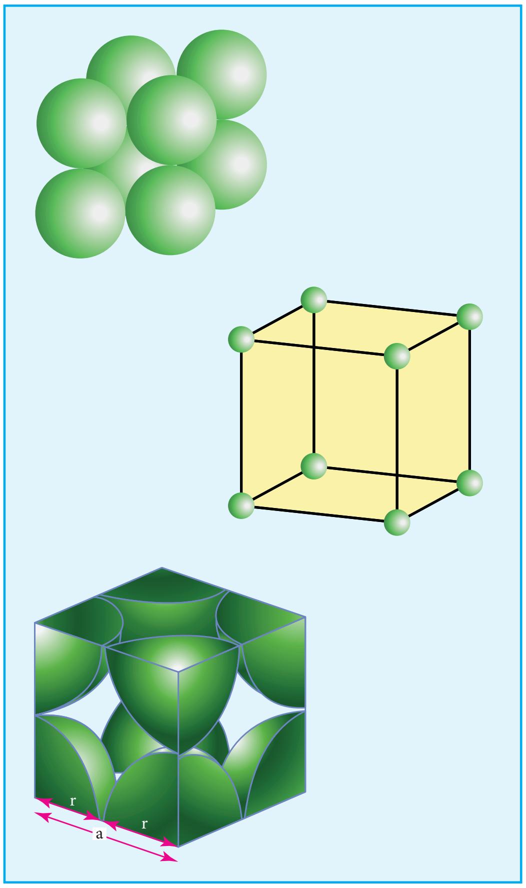
cubic	 primitive	 body centered	 face centered
tetragonal	 primitive	 body centered	
hexagonal			
orthorhombic	 primitive	 body centered	 face centered  basis face centered
monoclinic	 primitive		 basis face centered
trigonal			
triclinic			

Table 6.2 14 Bravais Lattices

Number of atoms in a cubic unit cell:

6.5.1 Primitive (or) simple cubic unit cell.(SC)



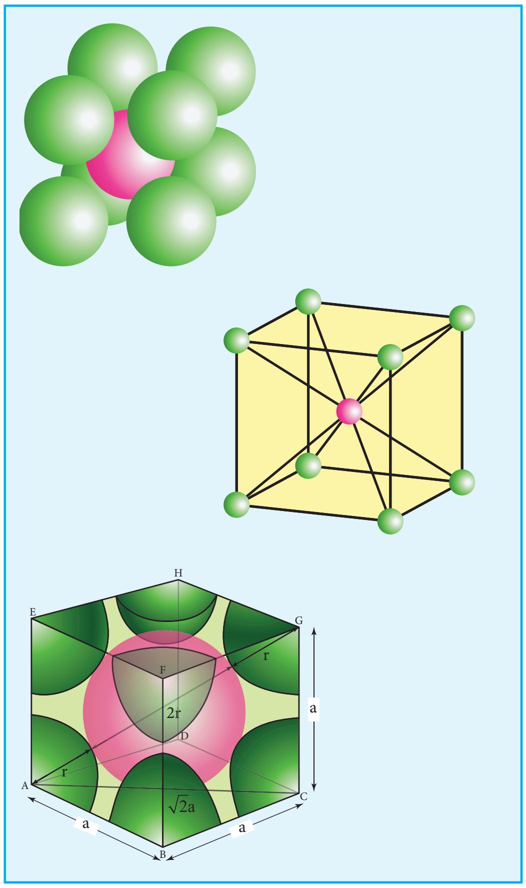
In the simple cubic unit cell, each corner is occupied by an identical atoms or ions or molecules. And they touch along the edges of the cube, do not touch diagonally. The coordination number of each atom is 6.

Each atom in the corner of the cubic unit cell is shared by 8 neighboring unit cells and therefore atoms `per unit cell is equal to $\frac{N_c}{8}$, where N_c is the number of atoms at the corners.

$$\therefore no\ of\ atoms\ in\ a\ \mathrm{SC}\ unit\ cell = \left(\frac{Nc}{8}\right)$$

$$= \left(\frac{8}{8}\right) = 1$$

6.5.2 Body centered cubic unit cell. (BCC)



In a body centered cubic unit cell, each corner is occupied by an identical particle and in addition to that one atom occupies the body centre. Those atoms which occupy the corners do not touch each other, however they all touch the one that occupies the body centre. Hence, each atom is surrounded by eight nearest neighbours and coordination number is 8. An atom present at the body centre belongs to only to a particular unit cell i.e unshared by other unit cell.

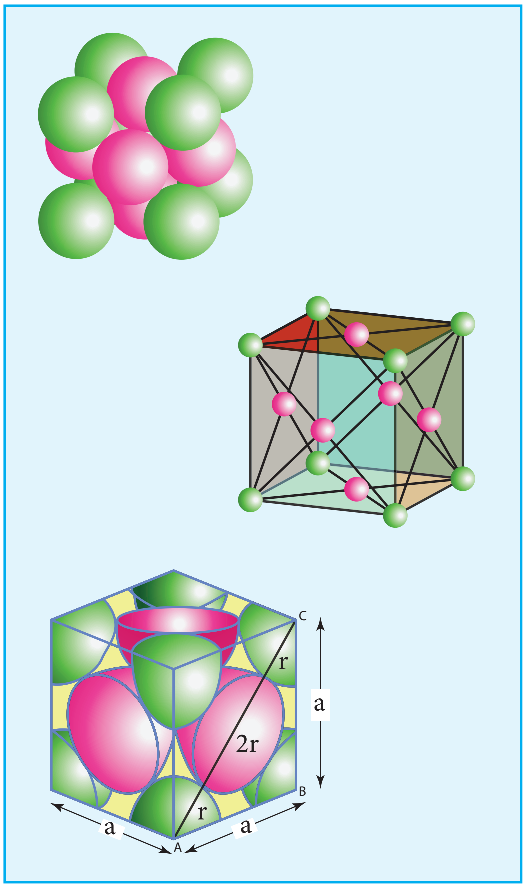
$$\therefore \text{Number of atoms in a bccunitcell} = \left(\frac{Nc}{8}\right) + \left(\frac{N_b}{1}\right)$$

$$= \left(\frac{8}{8} + \frac{1}{1}\right)$$

$$= (1+1)$$

$$= 2$$

6.5.3 Face centered cubic unit cell.(FCC)



In a face centered cubic unit cell, identical atoms lie at each corner as well as in the centre of each face. Those atoms in the corners touch those in the faces but not each other. The atoms in the face centre is being shared by two unit cells, each atom in the face centers makes $\left(\frac{1}{2}\right)$ contribution to the unit cell.

$$\therefore \text{Number of atoms in a fcc unitcell} = \left(\frac{N_c}{8}\right) + \left(\frac{N_f}{2}\right)$$

$$= \left(\frac{8}{8} + \frac{6}{2}\right)$$

$$= (1+3)$$

$$= 4$$

Drawing the crystal lattice on paper is not an easy task. The constituents in a unit cell touch each other and form a three dimensional network. This can be simplified by drawing crystal structure with the help of small circles (spheres) corresponding constituent particles and connecting neighbouring particles using a straight line as shown in the figure.

6.5.4 Calculations involving unit cell dimensions:

X-Ray diffraction analysis is the most powerful tool for the determination of crystal structure. The inter planar distance (d) between two successive planes of atoms can be calculated using the following equation form the X-Ray diffraction data

$$2d\sin\theta = n\lambda$$

The above equation is known as Bragg's equation.

Where

λ is the wavelength of X-ray used for diffraction.

θ is the angle of diffraction

By knowing the values of θ, λ and n we can calculate the value of d.

$$d = \frac{n\lambda}{2\sin\theta}$$

Using these values the edge of the unit cell can be calculated.

6.5.5 Calculation of density:

Using the edge length of a unit cell, we can calculate the density (ρ) of the crystal by considering a cubic unit cell as follows.

$$\text{Density of the unit cell} \quad \rho = \frac{\text{mass of the unit cell}}{\text{volume of the unit cell}} \qquad ...(1)$$

$$\text{mass of the unit cell} = \left\{\begin{array}{l}\text{total number of}\\ \text{atoms belongs to}\\ \text{that unit cell}\end{array}\right\} \times \left\{\begin{array}{l}\text{mass of}\\ \text{one atom}\end{array}\right\} \quad ...(2)$$

$$\text{mass of one atom} = \frac{\text{molar mass (gmol}^{-1})}{\text{Avagadro number (mol}^{-1})}$$

$$m = \frac{M}{N_A} \quad ...(3)$$

Substitute (3) in (2)

$$\text{mass of the unit cell} = n \times \frac{M}{N_A} \quad ...(4)$$

For a cubic unit cell, all the edge lengths are equal i.e , a=b=c

$$\text{volume of the unit cell} = a \times a \times a = a^3 \quad ...(5)$$

$$\therefore \textbf{Density of the unit cell } \rho = \frac{n\,M}{a^3 N_A} \quad ...(6)$$

Equation (6) contains four variables namely ρ , n , M and a . If any three variables are known, the fourth one can be calculated.

Example 2

Barium has a body centered cubic unit cell with a length of 508pm along an edge. What is the density of barium in g cm^{-3}?

Solution:

$$\rho = \frac{n\,M}{a^3 N_A}$$

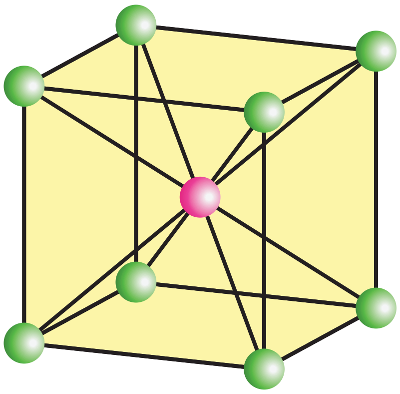
In this case,

n=2 ; M=137.3 gmol^{-1} ; a = 508pm= 5.08X10^{-8}cm

$$\rho = \frac{2 \text{ atoms} \times 137.3 \text{ g mol}^{-1}}{\left(5.08 \times 10^{-8}\text{ cm}\right)^3 \left(6.023 \times 10^{23}\text{ atoms mol}^{-1}\right)}$$

$$\rho = \frac{2 \times 137.3}{(5.08)^3 \times 10^{-24} \times 6.023 \times 10^{23}} \text{ g cm}^{-3}$$

$$\rho = 3.5 \text{ g cm}^{-3}$$



Evaluate yourself -1

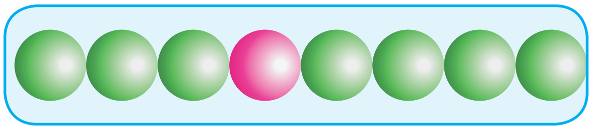
1. An element has a face centered cubic unit cell with a length of 352.4 pm along an edge. The density of the element is 8.9 gcm^{-3}. How many atoms are present in 100 g of an element?
2. Determine the density of CsCl which crystallizes in a bcc type structure with an edge length 412.1 pm.
3. A face centered cubic solid of an element (atomic mass 60) has a cube edge of $4\overset{0}{A}$. Calculate its density.

6.6 Packing in crystals:

Let us consider the packing of fruits for display in fruit stalls. They are in a closest packed arrangement as shown in the following fig. we can extend this analogy to visualize the packing of constituents (atoms / ions / molecules) in crystals, by treating them as hard spheres. To maximize the attractive forces between the constituents, they generally tend to pack together as close as possible to each other. In this portion we discuss how to pack identical spheres to create cubic and hexagonal unit cell. Before moving on to these three dimensional arrangements, let us first consider the two dimensional arrangement of spheres for better understanding.

6.6.1 Linear arrangement of spheres in one direction:

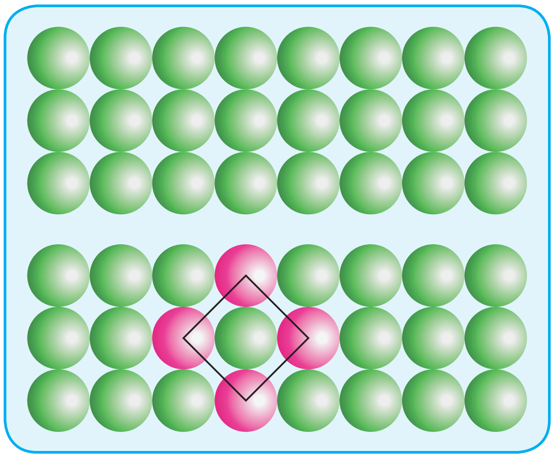
In a specific direction, there is only one possibility to arrange the spheres in one direction as shown in the fig. in this arrangement each sphere is in contact with two neighbouring spheres on either side.



6.6.2 Two dimensional close packing:

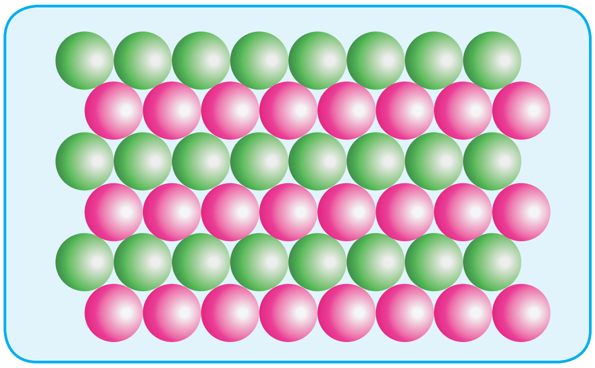
Two dimensional planar packing can be done in the following two different ways.

(i) AAA… type:



Linear arrangement of spheres in one direction is repeated in two dimension i.e., more number of rows can be generated identical to the one dimensional arrangement such that all spheres of different rows align vertically as well as horizontally as shown in the fig. If we denote the first row as A type arrangement, then the above mentioned packing is called AAA type, because all rows are identical as the first one. In this arrangement each sphere is in contact with four of its neighbours.

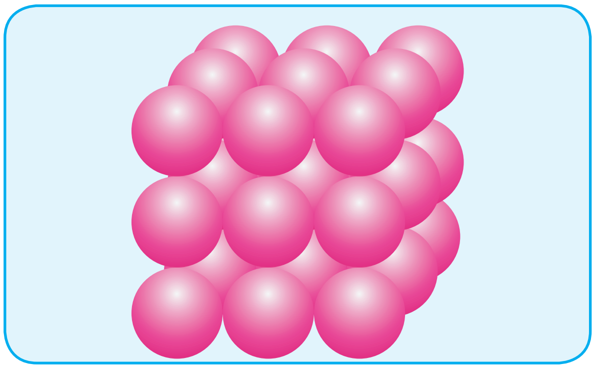
(i) ABAB.. Type:



In this type, the second row spheres are arranged in such a way that they fit in the depression of the first row as shown in the figure. The second row is denoted as B type. The third row is arranged similar to the first row A, and the fourth one is arranged similar to second one. i.e., the pattern is repeated as ABAB….In this arrangement each sphere is in contact with 6 of its neighbouring spheres.

On comparing these two arrangements (AAAA...type and ABAB….type) we found that the closest arrangement is ABAB…type.

6.6.3 Simple cubic arrangement:



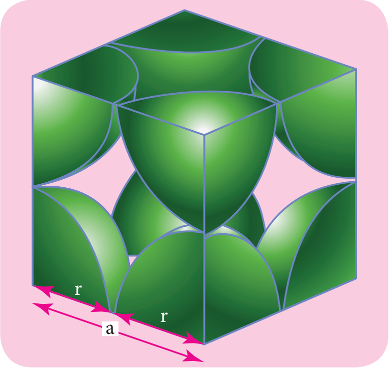
Simple Cubic (SC)

This type of three dimensional packing arrangements can be obtained by repeating the AAAA type two dimensional arrangements in three dimensions. i.e., spheres in one layer sitting directly on the top of those in the previous layer so that all layers are identical. All spheres of different layers of crystal are perfectly aligned horizontally and also vertically, so that any unit cell of such arrangement as simple cubic structure as shown in fig.

In simple cubic packing, each sphere is in contact with 6 neighbouring spheres - Four in its own layer, one above and one below and hence the coordination number of the sphere in simple cubic arrangement is 6.

Packing efficiency:

There is some free space between the spheres of a single layer and the spheres of successive layers. The percentage of total volume occupied by these constituent spheres gives the packing efficiency of an arrangement. Let us calculate the packing efficiency in simple cubic arrangement,



$$\left\{\begin{array}{l}\text{Packing fraction}\\ \text{(or) efficiency}\end{array}\right\} = \frac{\left\{\begin{array}{l}\text{Total volume occupied by}\\ \text{spheres in a unit cell}\end{array}\right\}}{\text{Volume of the unit cell}} \times 100$$

Let us consider a cube with an edge length ‘a’ as shown in fig.

Volume of the cube with edge length a is = $a \times a \times a = a^3$

Let ‘r’ is the radius of the sphere. From the figure, $a=2r \Rightarrow r = \frac{a}{2}$

∴ Volume of the sphere with radius 'r'

$$= \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi\left(\frac{a}{2}\right)^3$$

$$= \frac{4}{3}\pi\left(\frac{a^3}{8}\right)$$

$$= \frac{\pi a^3}{6} \qquad \ldots (1)$$

In a simple cubic arrangement, number of spheres belongs to a unit cell is equal to one

$$\therefore \text{Total volume occupied by the spheres in sc unit cell} = 1 \times \left(\frac{\pi a^3}{6}\right) \qquad \ldots (2)$$

Dividing (2) by (3)

$$\text{Packing fraction} = \frac{\left(\frac{\pi a^3}{6}\right)}{\left(a^3\right)} \times 100 = \frac{100\,\pi}{6}$$

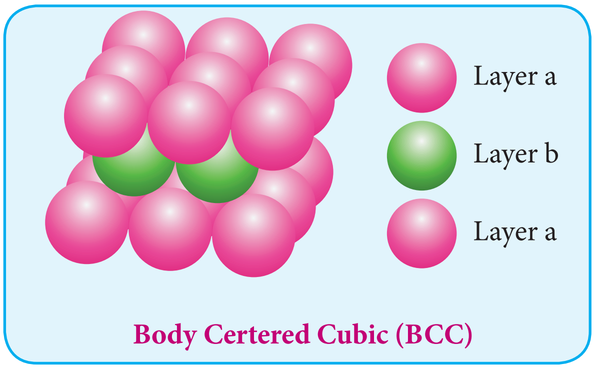
$$= 52.31\%$$

i.e., only 52.31% of the available volume is occupied by the spheres in simple cubic packing, making inefficient use of available space and hence minimizing the attractive forces.

More to know Of all the metals in the periodic table, only polonium crystallizes in simple cubic pattern.

6.6.4 Body centered cubic arrangement

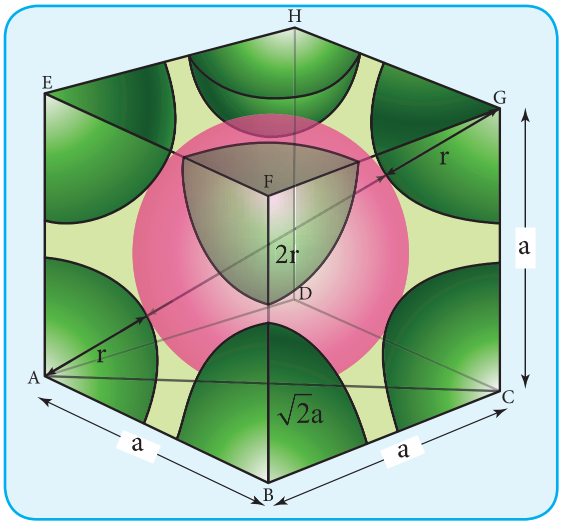
In this arrangement, the spheres in the first layer (A type) are slightly separated and the second layer is formed by arranging the spheres in the depressions between the spheres in layer A as shown in figure. The third layer is a repeat of the first. This pattern ABABAB is repeated throughout the crystal. In this arrangement, each sphere has a coordination number of 8, four neighbors in the layer above and four in the layer below.



Body Certered Cubic (BCC)

Packing efficiency:

Here, the spheres are touching along the leading diagonal of the cube as shown in the fig.



In ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC = \sqrt{AB^2 + BC^2}$$

$$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\,a$$

In ΔACG

$$AG^2 = AC^2 + CG^2$$

$$AG = \sqrt{AC^2 + CG^2}$$

$$AG = \sqrt{\left(\sqrt{2}a\right)^2 + a^2}$$

$$AG = \sqrt{2a^2 + a^2} = \sqrt{3a^2}$$

$$AG = \sqrt{3}\,a$$

i.e., $\sqrt{3}a = 4r$

$$r = \frac{\sqrt{3}}{4}a$$

∴ Volume of the sphere with radius 'r'

$$= \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3$$

$$= \frac{\sqrt{3}}{16}\pi a^3 \qquad \text{...(1)}$$

Number of spheres belong to a unit cell in bcc arrangement is equal to two and hence the total volume of all spheres

$$= 2 \times \left(\frac{\sqrt{3}\,\pi\, a^3}{16}\right) = \frac{\sqrt{3}\,\pi\, a^3}{8}$$

Dividing (2) by (3)

$$\text{Packing fraction} = \frac{\left(\frac{\sqrt{3}\,\pi\, a^3}{8}\right)}{\left(a^3\right)} \times 100$$

$$= \frac{\sqrt{3}\,\pi}{8} \times 100$$

$$= \sqrt{3}\,\pi \times 12.5$$

$$= 1.732 \times 3.14 \times 12.5$$

$$= 68\ \%$$

i.e., 68 % of the available volume is occupied. The available space is used more efficiently than in simple cubic packing.

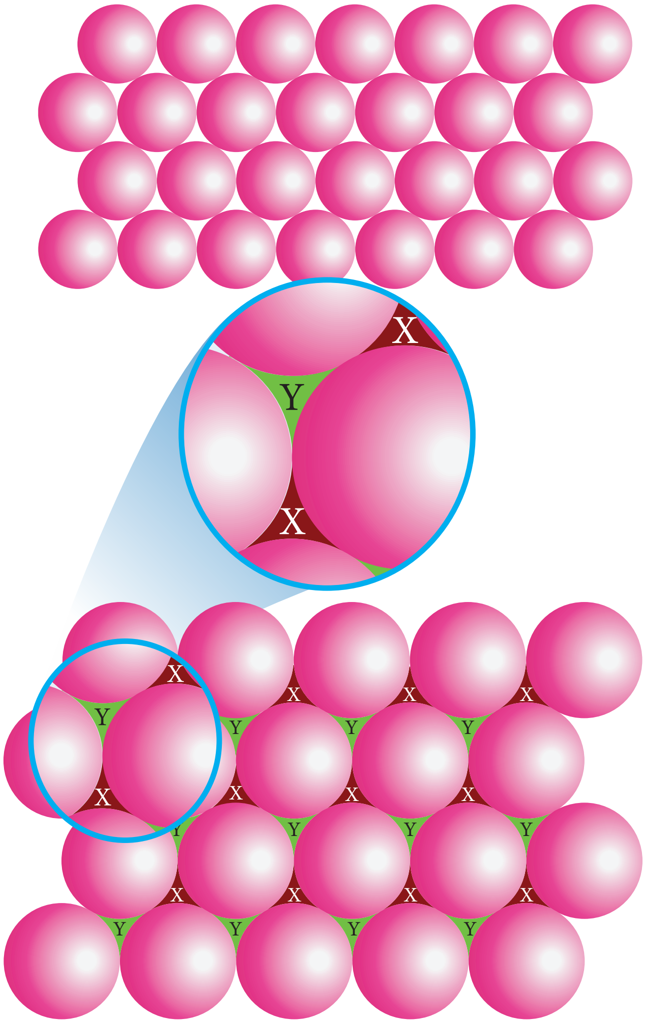
6.6.5 The hexagonal and face centered cubic arrangement:

Formation of first layer:

In this arrangement, the first layer is formed by arranging the spheres as in the case of two dimensional ABAB arrangements i.e. the spheres of second row fit into the depression of first row. Now designate this first layer as 'a'. The next layer is formed by placing the spheres in the depressions of the first layer. Let the second layer be 'b'.

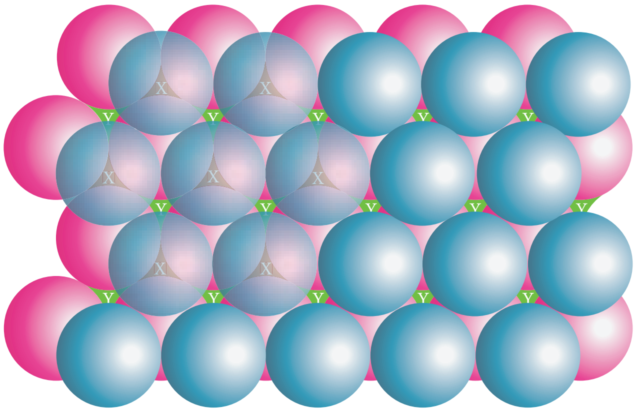
Formation of second layer:

In the first layer (a) there are two types of voids (or holes) and they are designated as x and y. The second layer (b) can be formed by placing the spheres either on the depression (voids/holes) x (or) on y. let us consider the formation of second layer by placing the spheres on the depression (x).



Wherever a sphere of second layer (b) is above the void (x) of the first layer (a), a tetrahedral void is formed. This constitutes four spheres – three in the lower (a) and one in the upper layer (b). When the centers of these four spheres are joined, a tetrahedron is formed.

At the same time, the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), now such a void in (a) is called a octahedral void. This constitutes six spheres – three in the lower layer (a) and three in the upper layer (b). When the centers of these six spheres are joined, an octahedron is formed. Simultaneously new tetrahedral voids (or holes) are also created by three spheres in second layer (b) and one sphere of first layer (a)



The number of voids depends on the number of close packed spheres. If the number of close packed spheres be ‘n’ then, the number of octahedral voids generated is equal to n and the number of tetrahedral voids generated is equal to 2n.

Formation of third layer:

The third layer of spheres can be formed in two ways to achieve closest packing

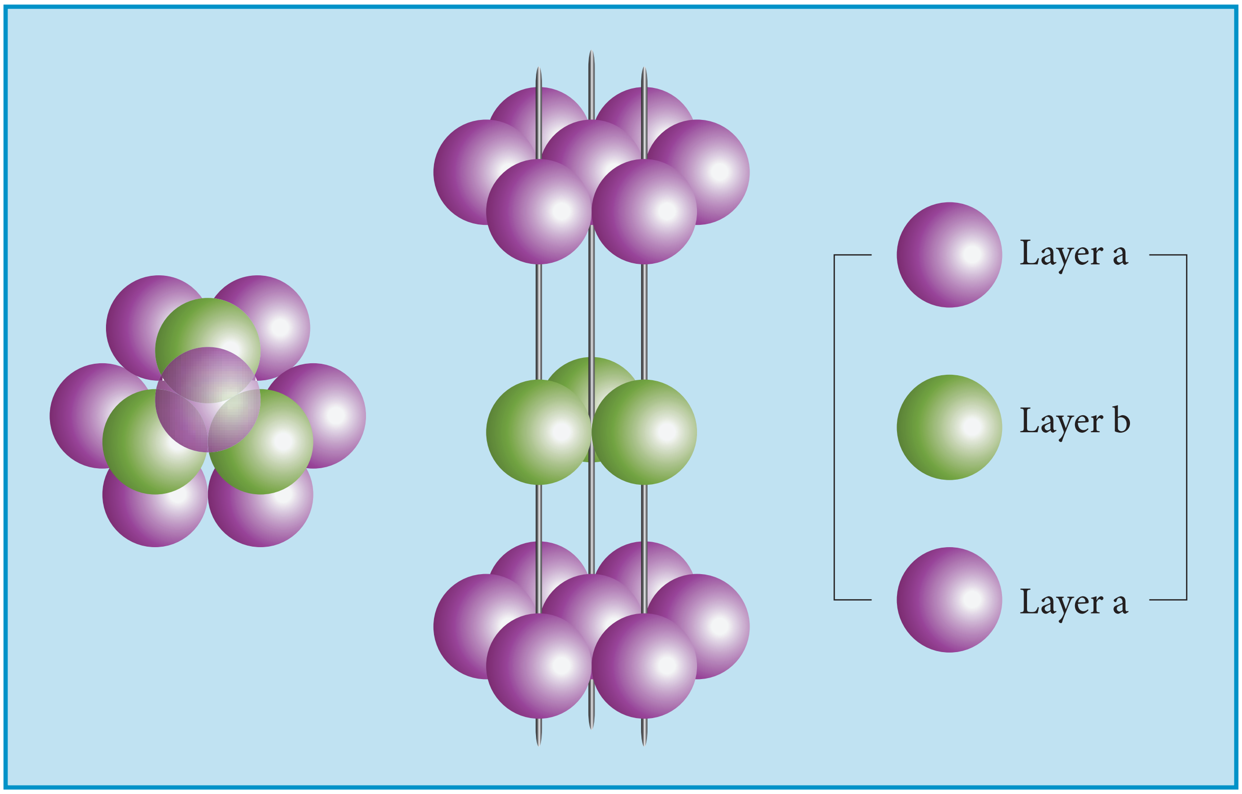
(i) aba arrangement - hcp structure

(ii) abc arrangement – ccp structure

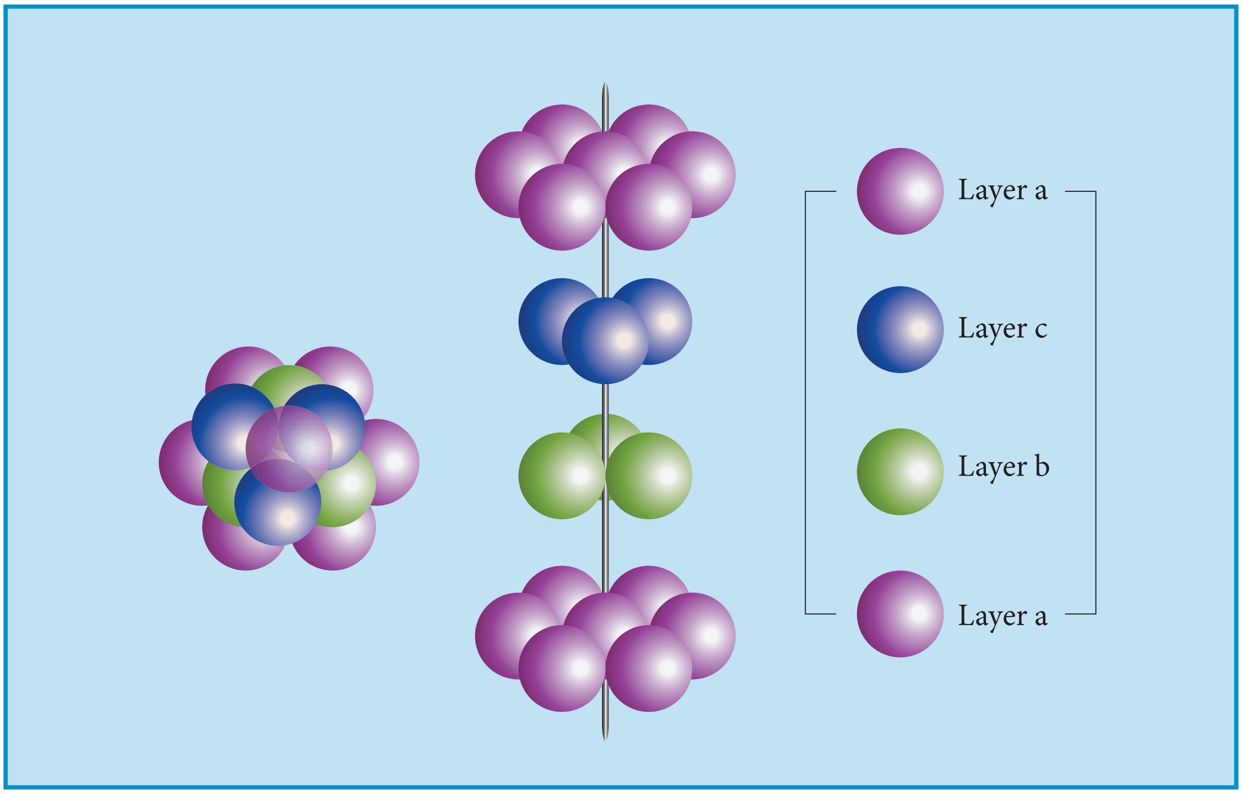
The spheres can be arranged so as to fit into the depression in such a way that the third layer is directly over a first layer as shown in the figure. This “aba” arrangement is known as the hexagonal close packed (hcp) arrangement. In this arrangement, the tetrahedral voids of the second layer are covered by the spheres of the third layer.

Alternatively, the third layer may be placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids. This arrangement of the third layer is different from other two layers (a) and (b), and hence, the third layer is designated (c). If the stacking of layers is continued in abcabcabc… pattern, then the arrangement is called cubic close packed (ccp) structure.

In both hcp and ccp arrangements, the coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and three sphere in the layer below. This is the most efficient packing.

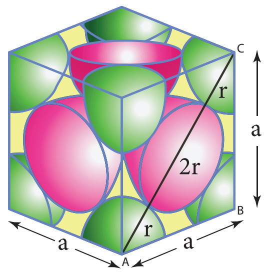


aba arrangement - hcp structure



abc arrangement – ccp structure

The cubic close packing is based on the face centered cubic unit cell. Let us calculate the packing efficiency in fcc unit cell.



From the figure

$$AC = 4r$$

$$4r = a\sqrt{2}$$

$$r = \frac{a\sqrt{2}}{4}$$

In ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC = \sqrt{AB^2 + BC^2}$$

$$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\,a$$

Volume of the sphere with radius r is

$$= \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3$$

$$= \frac{4}{3}\pi\left(\frac{2\sqrt{2}a^3}{64}\right)$$

$$= \frac{\sqrt{2}\,\pi a^3}{24}$$

Total number of spheres belongs to a single fcc unit cell is 4

∴ the volume of all spheres in a fcc unit cell

$$= 4 \times \left(\frac{\sqrt{2}\,\pi a^3}{24}\right)$$

$$= \left(\frac{\sqrt{2}\,\pi a^3}{6}\right)$$

$$\text{packing efficiency} = \frac{\left(\frac{\sqrt{2}\,\pi\, a^3}{6}\right)}{\left(a^3\right)} \times 100$$

$$= \frac{\sqrt{2}\,\pi}{6} \times 100$$

$$= \frac{1.414 \times 3.14 \times 100}{6}$$

$$= 74\%$$

Radius ratio:

The structure of an ionic compound depends upon the stoichiometry and the size of the ions.generally in ionic crystals the bigger anions are present in the close packed arrangements and the cations occupy the voids. The ratio of radius of cation and anion $\left(\frac{r_{C^+}}{r_{A^-}}\right)$ plays an important role in determining the structure. The following table shows the rleation between the radius ratio and the structural arrangement in ionic solids.

$\left(\frac{r_{C^+}}{r_{A^-}}\right)$	Coordination number	Structure	Example
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1.0	8	Cubic	CsCl

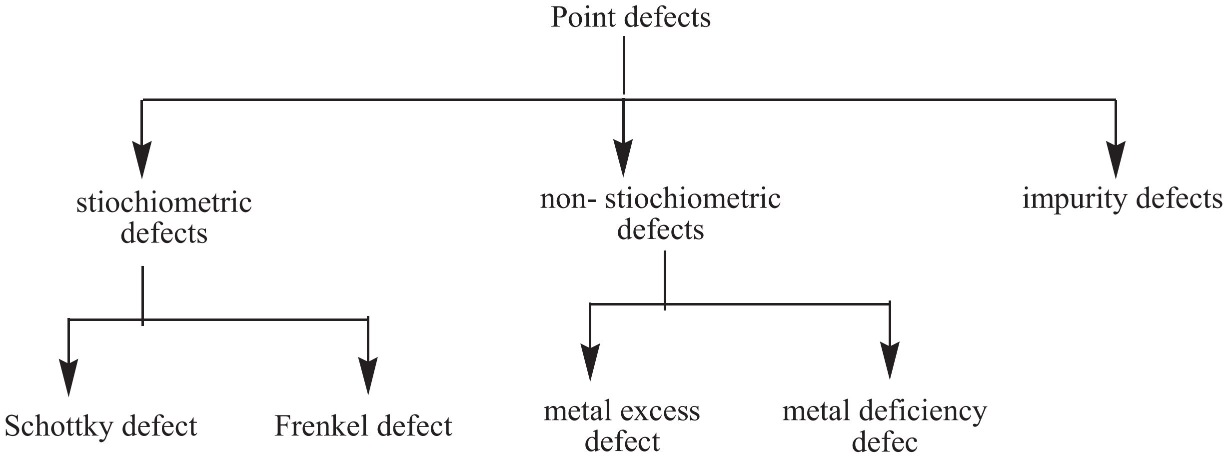
Table 6.3 Radius ratio

6.7 Imperfection in solids:

According to the law of nature nothing is perfect, and so crystals need not be perfect. They always found to have some defects in the arrangement of their constituent particles. These defects affect the physical and chemical properties of the solid and also play an important role in various processes. For example, a process called doping leads to a crystal imperfection and it increases the electrical conductivity of a semiconductor material such as silicon. The ability of ferromagnetic material such as iron, nickel etc., to be magnetized and demagnetized depends on the presence of imperfections. Crystal defects are classified as follows

1) Point defects
2) Line defects
3) Interstitial defects
4) Volume defects

In this portion, we concentrate on point defects, more specifically in ionic solids. Point defects are further classified as follows



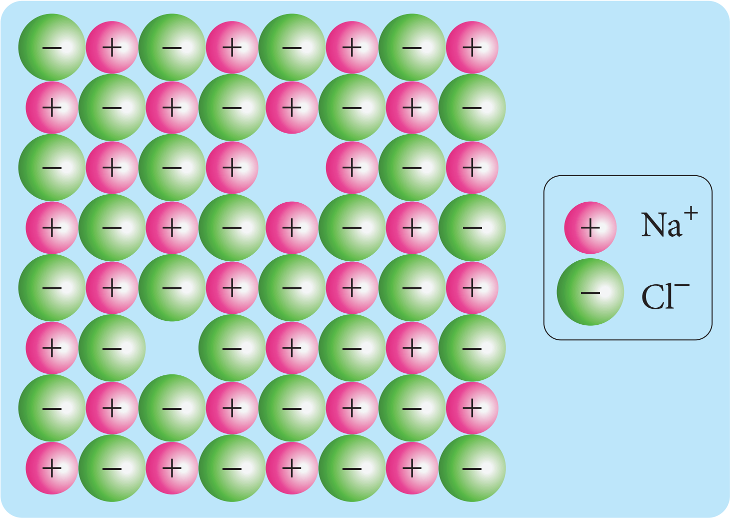
Stoichiometric defects in ionic solid:

This defect is also called intrinsic (or) thermodynamic defect. In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

6.7.1 Schottky defect:

Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice. This effect does not change the stoichiometry of the crystal. Ionic solids in which the cation and anion are of almost of similar size show schottky defect. Example: NaCl.

Presence of large number of schottky defects in a crystal, lowers

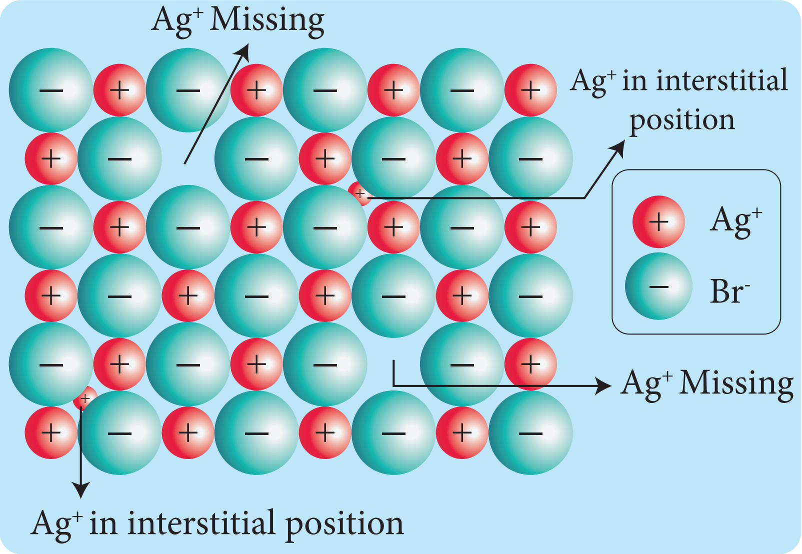


Schottky Defect

its density. For example, the theoretical density of vanadium monoxide (VO) calculated using the edge length of the unit cell is 6.5 g cm^{-3}, but the actual experimental density is 5.6 g cm^{-3}. It indicates that there is approximately 14% Schottky defect in VO crystal. Presence of Schottky defect in the crystal provides a simple way by which atoms or ions can move within the crystal lattice.

6.7.2 Frenkel defect:

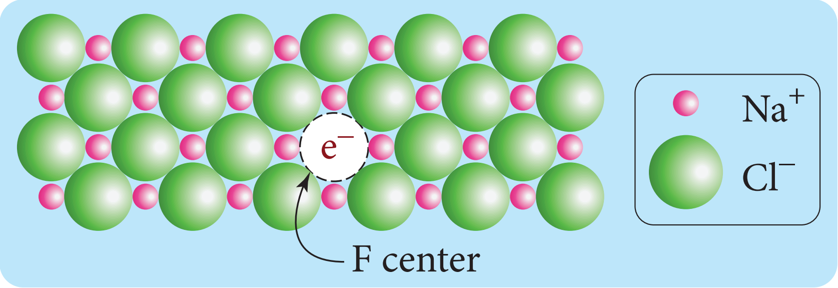
Frenkel defect arises due to the dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position. This defect is shown by ionic solids in which cation and anion differ in size. Unlike Schottky defect, this defect does not affect the density of the crystal. For example AgBr, in this case, small Ag$^+$ ion leaves its normal site and occupies an interstitial position as shown in the figure.



Frenkel Defect

6.7.3 Metal excess defect:

Metal excess defect arises due to the presence of more number of metal ions as compared to anions. Alkali metal halides NaCl, KCl show this type of defect. The electrical neutrality of the crystal can be maintained by the presence of anionic vacancies equal to the excess metal ions (or) by the presence of extra cation and electron present in interstitial position.



Metal Excess Defect

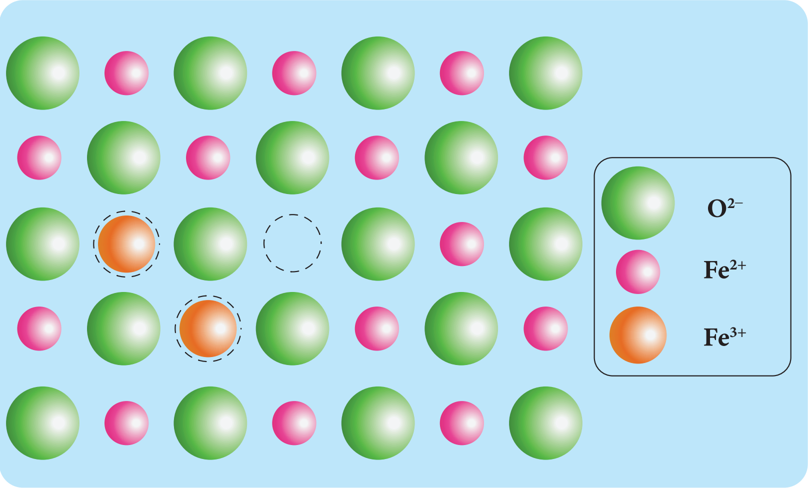
For example, when NaCl crystals are heated in the presence of sodium vapour, Na$^+$ ions are formed and are deposited on the surface of the crystal. Chloride ions (Cl$^-$) diffuse to the surface from the lattice point and combines with Na$^+$ ion. The electron lost by the sodium vapour diffuse into the crystal lattice and occupies the vacancy created by the Cl$^-$ ions. Such anionic vacancies which are occupied by unpaired electrons are called F centers. Hence, the formula of NaCl which contains excess Na$^+$ ions can be written as $Na_{1+x}Cl$.

ZnO is colourless at room temperature. When it is heated, it becomes yellow in colour. On heating, it loses oxygen and thereby forming free Zn^{2+} ions. The excess Zn^{2+} ions move to interstitial sites and the electrons also occupy the interstitial positions.

6.7.4 Metal deficiency defect:

Metal deficiency defect arises due to the presence of less number of cations than the anions. This defect is observed in a crystal in which, the cations have variable oxidation states.

For example, in FeO crystal, some of the Fe^{2+} ions are missing from the crystal lattice. To maintain the electrical neutrality, twice the number of other Fe^{2+} ions in the crystal is oxidized to Fe^{3+} ions. In such cases, overall number of Fe^{2+} and Fe^{3+} ions is less than the O^{2-} ions. It was experimentally found that the general formula of ferrous oxide is Fe_xO, where x ranges from 0.93 to 0.98.



Metal Deficiency Defect

6.7.5 Impurity defect:

A general method of introducing defects in ionic solids is by adding impurity ions. If the impurity ions are in different valance state from that of host, vacancies are created in the crystal lattice of the host. For example, addition of $CdCl_2$ to silver chloride yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag^+. This will disturb the electrical neutrality of the crystal. In order to maintain the same, proportional number of Ag^+ ions leaves the lattice. This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

DO YOU KNOW?

Energy harvesting by piezoelectric crystals:

Piezoelectricity (also called the piezoelectric effect) is the appearance of an electrical potential across the sides of a crystal when you subject it to mechanical stress. The word piezoelectricity means electricity resulting from pressure and latent heat. Even the inverse is possible which is known as inverse piezoelectric effect.

If you can make a little amount of electricity by pressing one piezoelectric crystal once, could youmake a significant amount by pressing many crystals over and over again? What happens if we bury piezoelectric crystals under streets to capture energy as vehicles pass by?

This idea, known as energy harvesting, has caught many people's interest. Even though there are limitations for the large-scale applications, you can produce electricity that is enough to charge your mobile phones by just walking. There are power generating footwears that has a slip-on insole with piezoelectric crystals that can produce enough electricity to charge batteries/ USB devices.`

Summary

- Solids have definite volume and shape.
- solids can be classified into the following two major types based on the arrangement of their constituents. (i) Crystalline solids (ii)Amorphous solids.
- A crystalline solid is one in which its constituents (atoms, ions or molecules), have an orderly arrangement extending over a long range.
- In contrast, in amorphous solids (In Greek, amorphous means no form) the constituents are randomly arranged.
- Crystalline solid is characterised by a definite orientation of atoms, ions or molecules, relative to one another in a three dimensional pattern. The regular arrangement of these species throughout the crystal is called a crystal lattice.
- A crystal may be considered to consist of large number of unit cells, each one in direct contact with its nearer neighbour and all similarly oriented in space.
- A unit cell is characterised by the three edge lengths or lattice constants a ,b and c and the angle between the edges α, β and γ
- There are seven primitive crystal systems; cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral. They differ in the arrangement of their crystallographic axes and angles. Corresponding to the above seven, Bravis defined 14 possible crystal systems
- In the simple cubic unit cell, each corner is occupied by an identical atoms or ions or molecules. And they touch along the edges of the cube, do not touch diagonally. The coordination number of each atom is 6.
- In a body centered cubic unit cell, each corner is occupied by an identical particle and in addition to that one atom occupies the body centre. Those atoms which occupy the corners do not touch each other, however they all touch the one that occupies the body centre. Hence, each atom is surrounded by eight nearest neighbours and coordination number is 8.
- In a face centered cubic unit cell, identical atoms lie at each corner as well as in the centre of each face. Those atoms in the corners touch those in the faces but

not each other.The coordination number is 2.

- X-Ray diffraction analysis is the most powerful tool for the determination of crystal structure. The inter planar distance (d) between two successive planes of atoms can be calculated using the following equation form the X-Ray diffraction data $2d\sin\theta = n\lambda$
- The structure of an ionic compound depends upon the stoichiometry and the size of the ions.generally in ionic crystals the bigger anions are present in the close packed arrangements and the cations occupy the voids. The ratio of radius of cation and anion $\left(\frac{r_{C^+}}{r_{A^-}}\right)$ plays an important role in determining the structure
- Crystals always found to have some defects in the arrangement of their constituent particles.
- Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice.
- Frenkel defect arises due to the dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position.
- Metal excess defect arises due to the presence of more number of metal ions as compared to anions.
- Metal deficiency defect arises due to the presence of less number of cations than the anions.

EVALUATION

JN28IA

Choose the best answer:

1. Graphite and diamond are

   a) Covalent and molecular crystals　　b) ionic and covalent crystals

   c) both covalent crystals　　d) both molecular crystals

2. An ionic compound A_xB_y crystallizes in fcc type crystal structure with B ions at the centre of each face and A ion occupying entre of the cube. the correct formula of AxBy is

   a) AB　　b) AB_3

   c) A_3B　　d) A_8B_6

3. The ratio of close packed atoms to tetrahedral hole in cubic packing is

   a) 1:1　　b) 1:2

   c) 2:1　　d) 1:4

4. Solid CO_2 is an example of

a) Covalent solid b) metallic solid

c) molecular solid d) ionic solid

5. Assertion : monoclinic sulphur is an example of monoclinic crystal system

Reason: for a monoclinic system, $a \neq b \neq c$ and $\alpha = \gamma = 90^0, \beta \neq 90^0$

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false.

6. In calcium fluoride, having the flurite structure the coordination number of Ca^{2+} ion and F^- Ion are (NEET)

a) 4 and 2 b) 6 and 6

c) 8 and 4 d) 4 and 8

7. The number of unit cells in 8 gm of an element X (atomic mass 40) which crystallizes in bcc pattern is (N_A is the Avogadro number)

a) $6.023 \text{ X } 10^{23}$ b) $6.023 \text{ X } 10^{22}$

c) $60.23 \text{ X } 10^{23}$ d) $\left(\frac{6.023 \times 10^{23}}{8 \times 40}\right)$

8. The number of carbon atoms per unit cell of diamond is

a) 8 b) 6 c) 1 d) 4

9. In a solid atom M occupies ccp lattice and $\left(\frac{1}{3}\right)$ of tetrahedral voids are occupied by atom N. find the formula of solid formed by M and N.

a) MN b) M_3N c) MN_3 d) M_3N_2

10. The composition of a sample of wurtzite is $Fe_{0.93}O_{1.00}$ what % of Iron present in the form of Fe^{3+}?

a) 16.05% b) 15.05% c) 18.05% d) 17.05%

11. The ionic radii of A^+ and B^- are 0.98×10^{-10}m and 1.81×10^{-10}m . the coordination number of each ion in AB is

a) 8 b) 2 c) 6 d) 4

12. CsCl has bcc arrangement, its unit cell edge length is 400pm, its inter atomic distance is

a) 400pm b) 800pm c) $\sqrt{3} \times 100$pm d) $\left(\frac{\sqrt{3}}{2}\right) \times 400$pm

13. A solid compound XY has NaCl structure. if the radius of the cation is 100pm , the radius of the anion will be

a) $\left(\frac{100}{0.414}\right)$ b) $\left(\frac{0.732}{100}\right)$ c) 100×0.414 d) $\left(\frac{0.414}{100}\right)$

14. The vacant space in bcc lattice unit cell is

a) 48% b) 23% c) 32% d) 26%

15. The radius of an atom is 300pm, if it crystallizes in a face centered cubic lattice, the length oif the edge of the unit cell is

a) 488.5pm b) 848.5pm c) 884.5pm d) 484.5pm

16. The fraction of total volume occupied by the atoms in a simple cubic is

a) $\left(\frac{\pi}{4\sqrt{2}}\right)$ b) $\left(\frac{\pi}{6}\right)$ c) $\left(\frac{\pi}{4}\right)$ d) $\left(\frac{\pi}{3\sqrt{2}}\right)$

17. The yellow colour in NaCl crystal is due to

a) excitation of electrons in F centers

b) reflection of light from Cl^- ion on the surface

c) refraction of light from Na^+ ion

d) all of the above

18. if ‘a’ stands for the edge length of the cubic system ; sc , bcc, and fcc. Then the ratio of radii of spheres in these systems will be respectively.

a) $\left(\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a\right)$ b) $\left(\sqrt{1}a : \sqrt{3}a : \sqrt{2}a\right)$

c) $\left(\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a\right)$ d) $\left(\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a\right)$

19. If ‘a’ is the length of the side of the cube, the distance between the body centered atom and one corner atom in the cube will be

a) $\left(\frac{2}{\sqrt{3}}\right)a$ b) $\left(\frac{4}{\sqrt{3}}\right)a$

c) $\left(\frac{\sqrt{3}}{4}\right)a$ d) $\left(\frac{\sqrt{3}}{2}\right)a$

20. Potassium has a bcc structure with nearest neighbor distance 4.52 A^0 . its atomic weight is 39. its density will be

a) 915 kg m^{-3} b) 2142 kg m^{-3} c) 452 kg m^{-3} d) 390 kg m^{-3}

21. Schottky defect in a crystal is observed when

a) unequal number of anions and anions are missing from the lattice

b) equal number of anions and anions are missing from the lattice

c) an ion leaves its normal site and occupies an interstitial site

d) no ion is missing from its lattice.

22. The cation leaves its normal position in the crystal and moves to some interstitial position, the defect in the crystal is known as

a) Schottky defect	b) F center
c) Frenkel defect	d) non-stoichiometric defect

23. Assertion: due to Frenkel defect, density of the crystalline solid decreases.

Reason: in Frenkel defect cation and anion leaves the crystal.

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

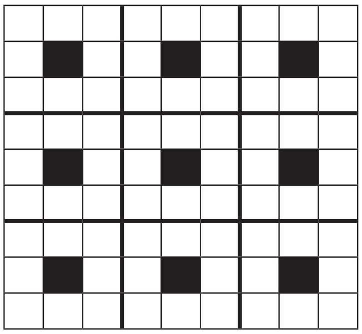
c) Assertion is true but reason is false.

d) Both assertion and reason are false

24. The crystal with a metal deficiency defect is

a) NaCl	b) FeO
c) ZnO	d) KCl

25. A two dimensional solid pattern formed by two different atoms X and Y is shown below. The black and white squares represent atoms X and Y respectively. the simplest formula for the compound based on the unit cell from the pattern is



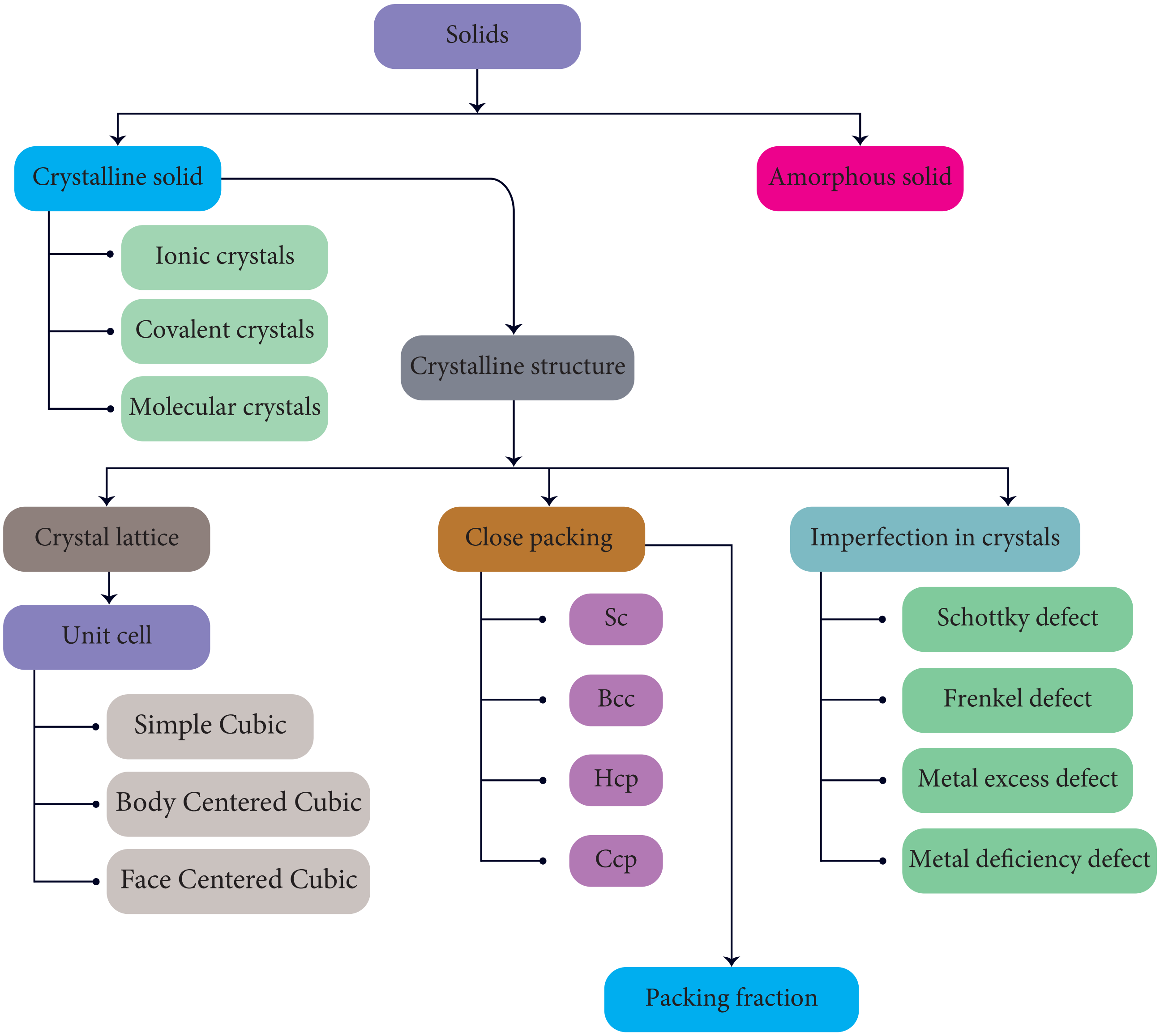
a) XY_8	b) X_4Y_9
c) XY_2	d) XY_4

Answer the following questions:

1. Define unit cell.
2. Give any three characteristics of ionic crystals.
3. Differentiate crystalline solids and amorphous solids.
4. Classify the following solids

a. P_4 b. Brass c. diamond d. NaCl e. Iodine

5. Explain briefly seven types of unit cell.
6. Distinguish between hexagonal close packing and cubic close packing.
7. Distinguish tetrahedral and octahedral voids.
8. What are point defects?
9. Explain Schottky defect.
10. Write short note on metal excess and metal deficiency defect with an example.
11. Calculate the number of atoms in a fcc unit cell.
12. Explain AAAA and ABABA and ABCABC type of three dimensional packing with the help of neat diagram.
13. Why ionic crystals are hard and brittle?
14. Calculate the percentage efficiency of packing in case of body centered cubic crystal.
15. What is the two dimensional coordination number of a molecule in square close packed layer?
16. Experiment shows that Nickel oxide has the formula $Ni_{0.96}O_{1.00}$. What fraction of Nickel exists as of Ni^{2+} and Ni^{3+} ions?
17. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure?
18. An element has bcc structure with a cell edge of 288 pm. the density of the element is 7.2 gcm^{-3}. how many atoms are present in 208g of the element.
19. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125pm. calculate the edge length of unit cell.
20. if NaCl is doped with 10^{-2} mol percentage of strontium chloride, what is the concentration of cation vacancy?
21. KF crystallizes in fcc structure like sodium chloride. calculate the distance between K^+ and F^- in KF.(given : density of KF is $2.48\ g\ cm^{-3}$)
22. An atom crystallizes in fcc crystal lattice and has a density of $10\ gcm^{-3}$ with unit cell edge length of 100pm. calculate the number of atoms present in 1 g of crystal.
23. Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube and Y is at the centre of the cube. What is the formula of the compound?
24. Sodium metal crystallizes in bcc structure with the edge length of the unit cell $4.3\times10^{-8}\,cm$. calculate the radius of sodium atom.
25. Write a note on Frenkel defect.


Solids
Crystalline solid
Amorphous solid
Ionic crystals
Covalent crystals
Molecular crystals
Crystalline structure
Crystal lattice
Close packing
Imperfection in crystals
Unit cell
Simple Cubic
Body Centered Cubic
Face Centered Cubic
Sc
Bcc
Hcp
Ccp
Schottky defect
Frenkel defect
Metal excess defect
Metal deficiency defect
Packing fraction

ICT Corner

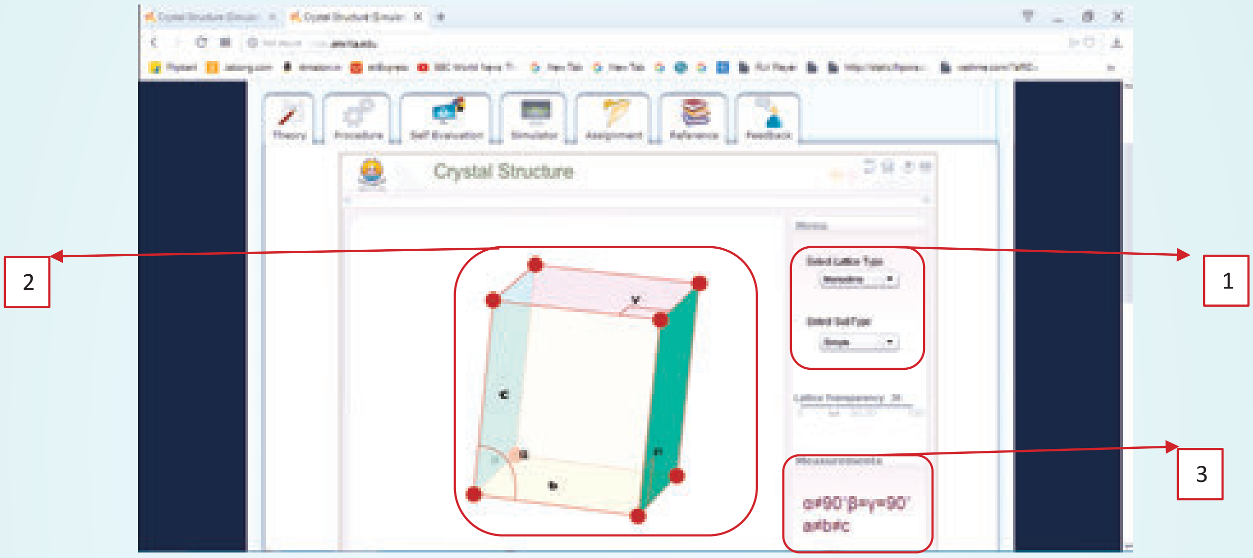
CRYSTAL SYSTEMS

By using this tool, you will be able to visualize different crystal systems and know their unit cell parameters.

Please go to the URL
http://vlab.amrita.edu
(or) Scan the QR code on the right side

Steps

- Open the Browser and type the URL given (or) Scan the QR Code. In the webpage click physical science tab and then click solid state virtual lab. Then go to crystal structure and then click simulator.
  Note: *One time sign up is needed to access this webpage. Login using your username and password. Once logged in click the simulator tab.*
- Now the using the menu (box 1) select any one of the seven crystal systems and the lattice type. Now the unit cell of the selected crystal system will appear on screen (box 2) and the unit cell parameters will also be displayed in the measurement tab (box 3)

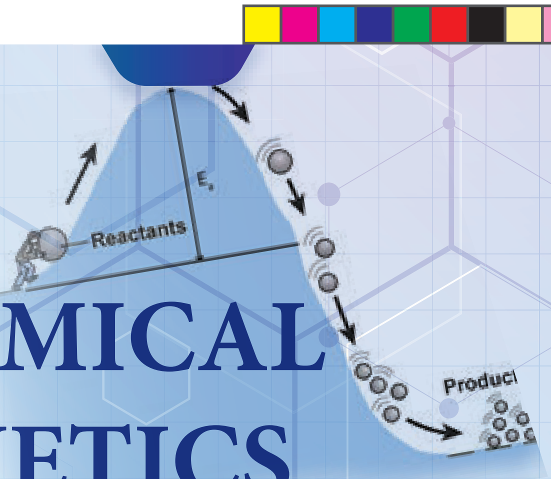


α≠90° β=γ=90°
a≠b≠c

B264_12_CHEMISTRY_EM

UNIT 7

CHEMICAL KINETICS



**Svante August Arrhenius
(1859 –1927)**

Svante August Arrhenius was a Swedish scientist. Arrhenius was one of the founders of the science of physical chemistry. He focused his attention on the conductivities of electrolytes. He proposed that crystalline salts dissociate into paired charged ions when dissolved in water, for which he received the Nobel Prize for Chemistry in 1903. He also proposed definitions for acids and bases. He formulated the concept of activation energy.

WJN386

Learning Objectives

After studying this unit, the students will be able to

- define the rate and order of a reaction,
- derive the integrated rate equations for zero and first order reactions,
- describe the half life period,
- describe the collision theory,
- discuss the temperature dependence of the rate of a reaction, and
- explain various factors which affect the rate of a reaction.

INTRODUCTION

We have already learnt in XI standard that the feasibility of a chemical reaction under a given set of conditions can be predicted, using the principles of thermodynamics. However, thermodynamics does not provide an answer to a very important question of how fast a chemical reaction takes place. We know from our practical experience that all chemical reactions take some time for completion. Reaction speeds ranging from extremely fast (in femto seconds) to extremely slow (in years). For example, when the reactants $BaCl_2$ solution and dilute H_2SO_4 are just mixed, a white precipitate of $BaSO_4$ is immediately formed; on the other hand reactions such as rusting of Iron take many years to complete. The answers to the questions such as (i) how fast a chemical change can occur and (ii) What happens in a chemical reaction during the period between the initial stage and final stage are provided by the chemical kinetics. The word kinetics is derived from the Greek word "kinesis" meaning movement.

Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.

The study of chemical kinetics not only help us to determine the rate of a chemical reaction, but also useful in optimizing the process conditions of industrial manufacturing processes, organic and inorganic synthesis etc.

In this unit, we discuss the rate of a chemical reaction and the factors affecting it. We also discuss the theories of the reaction rate and temperature dependence of a chemical reaction.

7.1 Rate of a chemical reaction:

A rate is a change in a particular variable per unit time. You have already learnt in physics that change in the displacement of a particle per unit time gives its velocity. Similarly in a chemical reaction, the change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

Let us consider a simple general reaction

$$A \longrightarrow B$$

The concentration of the reactant ([A]) can be measured at different time intervals. Let the concentration of A at two different times t_2 and t_2, $(t_2>t_1)$ be $[A_1]$ and $[A_2]$ respectively. The rate of the reaction can be expressed as

$$\text{Rate} = \frac{-\text{[Change in the concentration of the reactants]}}{\text{(Change in time)}}$$

$$\text{i.e., Rate} = \frac{-([A_2]-[A_1])}{(t_2-t_1)} = -\left(\frac{\Delta[A]}{\Delta t}\right) \quad ...(7.1)$$

During the reaction, the concentration of the reactant decreases i.e. $[A_2]<[A_1]$ and hence the change in concentration $[A_2]-[A_1]$ gives a negative value. By convention the reaction rate is a positive one and hence a negative sign is introduced in the rate expression (equation 7.1)

If the reaction is followed by measuring the product concentration, the rate is given by $\left(\frac{\Delta[B]}{\Delta t}\right)$ since $[B_2]>[B_1]$, no minus sign is required here.

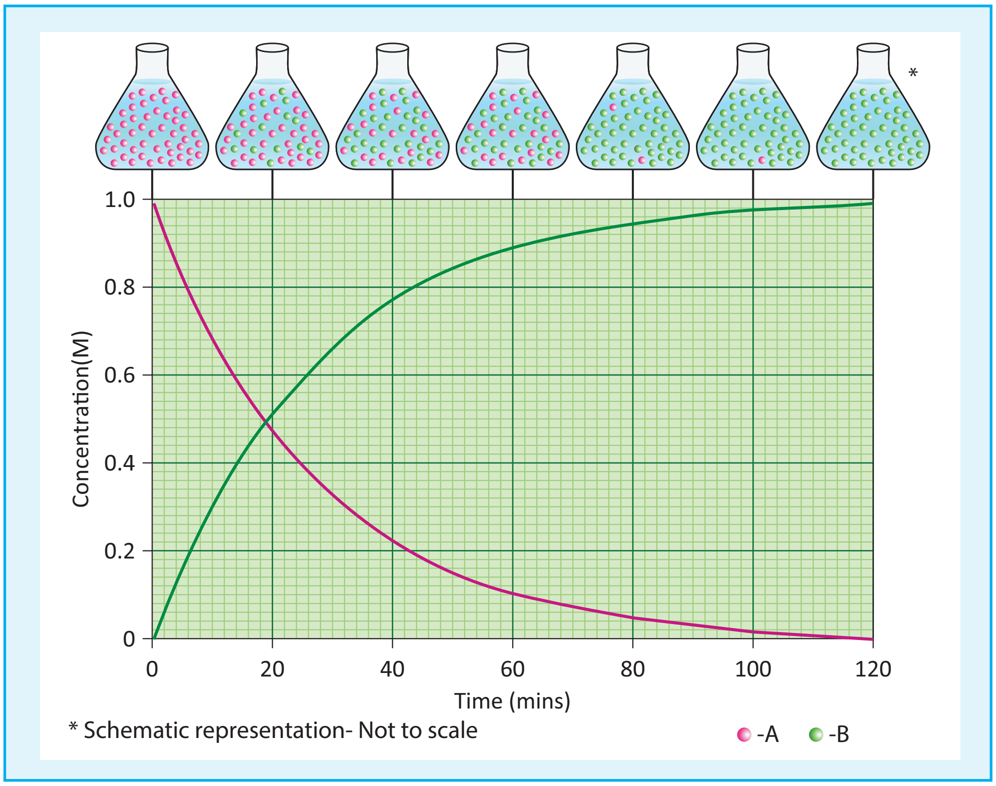


Fig 7.1 change in concentration of A and B for the reaction $A \longrightarrow B$

Unit of rate of a reaction:

$$\text{unit of rate} = \frac{\text{unit of concentration}}{\text{unit of time}}$$

Usually, concentration is expressed in number of moles per litre and time is expressed in seconds and therefore the unit of the rate of a reaction is $\text{mol L}^{-1}\text{s}^{-1}$. Depending upon the nature of the reaction, minute, hour, year etc can also be used.

For a gas phase reaction, the concentration of the gaseous species is usually expressed in terms of their partial pressures and in such cases the unit of reaction rate is atm s^{-1}.

7.1.1 Stoichiometry and rate of a reaction:

In a reaction $A \longrightarrow B$, the stoichiometry of both reactant and product are same, and hence the rate of disappearance of reactant (A) and the rate of appearance of product (B) are same.

Now, let us consider a different reaction

$$A \longrightarrow 2B$$

In this case, for every mole of A, that disappears two moles of B appear, i.e., the rate of formation of B is twice as fast as the rate of disappearance of A. therefore, the rate of the reaction can be expressed as below

$$\text{Rate} = \frac{+\,d[B]}{dt} = 2\left(\frac{-d[A]}{dt}\right)$$

In other words,

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$

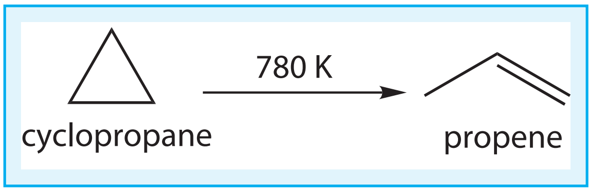
For a general reaction, the rate of the reaction is equal to the rate of consumption of a reactant (or formation of a product) divided by its coefficient in the balanced equation

$$xA + yB \longrightarrow lC + mD$$

$$\text{Rate} = \frac{-1}{x}\frac{d[A]}{dt} = \frac{-1}{y}\frac{d[B]}{dt} = \frac{1}{l}\frac{d[C]}{dt} = \frac{1}{m}\frac{d[D]}{dt}$$

7.1.2 Average and instantaneous rate:

Let us understand the average rate and instantaneous rate by considering the isomerisation of cyclopropane.



The kinetics of the above reaction is followed by measuring the concentration of cyclopropane at regular intervals and the observations are shown below. (Table 7.1)

Table 7.1 Concentration of cyclopropane at various times during its isomerisation at 780K

Time (min)	[cyclopropane] (mol L^{-1})
0	2.00
5	1.67
10	1.40
15	1.17
20	0.98
25	0.82
30	0.69

$$\text{Rate of the reaction} = \frac{-\Delta\,[\text{cyclopropane}]}{\Delta t}$$

$$\begin{matrix}\text{The rate over the}\\ \text{entire 30 min}\end{matrix} = \frac{-(0.69-2)\ \text{mol}L^{-1}}{(30-0)\ \text{min}}$$

$$= \frac{1.31}{30} = 4.36 \times 10^{-2}\ \text{mol}L^{-1}\text{min}^{-1}$$

It means that during the first 30 minutes of the reaction, the concentration of the reactant (cyclo propane) decreases as an average of 4.36×10^{-2} mol L^{-1}each minute.

Let us calculate the average rate for an initial and later stage over a short period.

$$(\text{Rate})_{\substack{\text{initial}\\ \text{stage}}} = \frac{-(2.0-1.4)}{(10-0)}$$

$$= \frac{0.6}{10} = 6 \text{ x } 10^{-2}\ \text{mol } L^{-1}\ \text{min}^{-1}$$

$$(\text{Rate})_{\substack{\text{later}\\ \text{stage}}} = \frac{-(\,0.69 - 0.98)}{(30\text{-}20)}$$

$$= \frac{0.29}{10} = 2.9 \text{ x } 10^{-2}\ \text{mol } L^{-1}\text{min}^{-1}$$

From the above calculations, we come to know that the rate decreases with time as the reaction proceeds and the average rate cannot be used to predict the rate of the reaction at any instant. The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,

As $\Delta t \rightarrow 0$;

$$\frac{-\Delta[\text{cyclopropane}]}{\Delta t} = \frac{-d[\text{cyclopropane}]}{dt}$$

A plot of [cyclopropane] Vs (time) gives a curve as shown in the figure 7.2. Instantaneous rate at a particular instant ‘t ’ $\frac{-d\,[\text{cyclopropane}]}{dt}$ is obtained by calculating the slope of a tangent drawn to the curve at that instant.

In general, the instantaneous reaction rate at a moment of mixing the reactants is calculated from the slope of the tangent drawn to the curve at mol L^{-1}, the rate calculated by this method is called initial rate of a reaction.

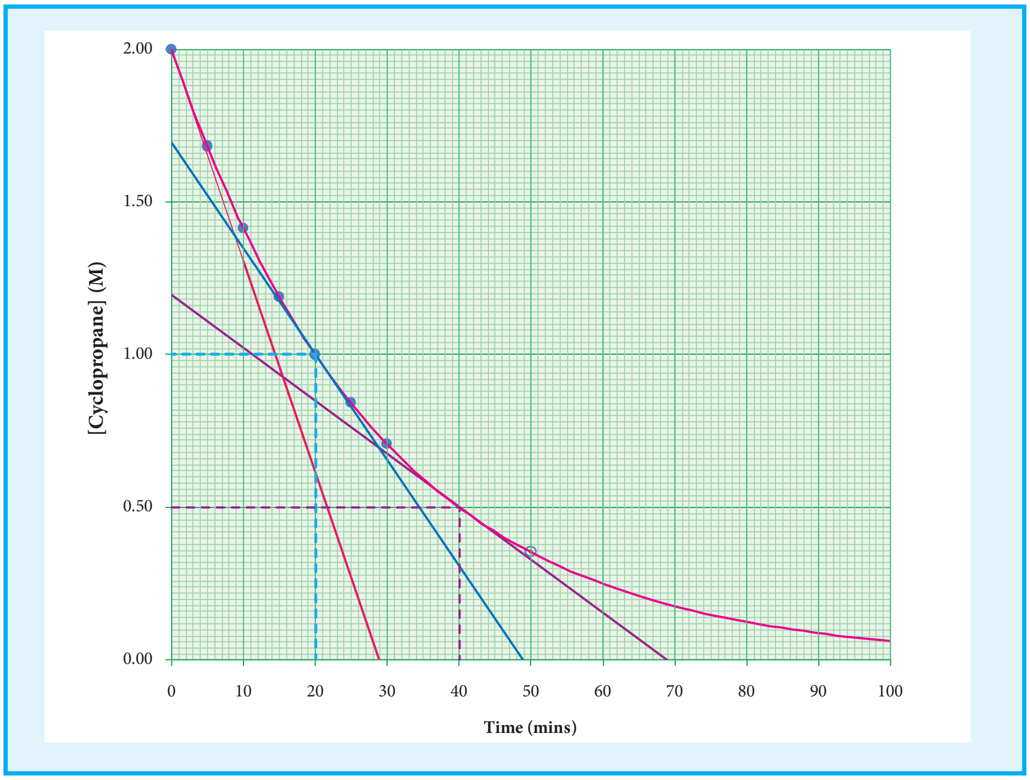


Fig 7.2 Concentration of cyclopropane vs time - graph

Let us calculate the instantaneous rate of isomerisation cyclopropane at different concentrations: 2 M, 1M and 0.5 M from the graph shown in fig 7.2, the results obtained are tabulated below.

[cyclopropane] mol L^{-1}	Rate mol $L^{-1}min^{-1}$
2	6.92×10^{-2}
1	3.46×10^{-2}
0.5	1.73×10^{-2}

Table 7.2 Rate of isomerisation

7.3 Rate law and rate constant:

We have just learnt that, the rate of the reaction depends upon the concentration of the reactant. Now let us understand how the reaction rate is related to concentration by considering the following general reaction.

$$xA + yB \longrightarrow \text{products}$$

The rate law for the above reaction is generally expressed as

$$\text{Rate} = k\,[A]^m[B]^n$$

Where k is proportionality constant called the rate constant. The values of m and n represent the reaction order with respect to A and B respectively. The overall order of the reaction is given by (m+n). The values of the exponents (m and n) in the rate law must be determined by experiment. They cannot be deduced from the Stoichiometry of the reaction. For example, consider the isomerisation of cyclopropane, that we discussed earlier.

The results shown in table 7.2 indicate that if the concentration of cyclopropane is reduced to half, the rate also reduced to half. It means that the rate depends upon [cyclopropane] raised to the first power

i.e., $\text{Rate} = k[\text{cyclopropane}]^1$

$$\Rightarrow \frac{\text{Rate}}{[\text{cyclopropane}]} = k$$

Table 7.3 Rate constant for isomerisation

Rate mol $L^{-1}min^{-1}$	[cyclopropane] mol L^{-1}	$k = \frac{\text{Rate}}{[\text{cyclopropane}]}$
6.92×10^{-2}	2	3.46×10^{-2}
3.46×10^{-2}	1	3.46×10^{-2}
1.73×10^{-2}	0.5	3.46×10^{-2}

Let us consider an another example, the oxidation of nitric oxide (NO)

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

Series of experiments are conducted by keeping the concentration of one of the reactants constant and the changing the concentration of the others.

Experiment	[NO] X 10^{-2} (mol L^{-1})	[O_2] X 10^{-2} (mol L^{-1})	Initial rate x 10^{-2} (mol $L^{-1}min^{-1}$)
1	1.3	1.1	19.26
2	1.3	2.2	38.40
3	2.6	1.1	76.80

$$\text{Rate} = k\,[NO]^m[O_2]^n$$

For experiment 1, the rate law is

$$\text{Rate}_1 = k\,[NO]^m[O_2]^n$$

$$19.26\ X10^{-2} = k\,[1.3]^m[1.1]^n \qquad ...(1)$$

Similarly for experiment 2

$$\text{Rate}_2 = k\,[NO]^m[O_2]^n$$

$$38.40\ X10^{-2} = k\,[1.3]^m[2.2]^n \qquad ...(2)$$

For experiment 3

$$\text{Rate}_3 = k\,[NO]^m[O_2]^n$$

$$76.8 \times 10^{-2} = k\,[2.6]^m[1.1]^n \qquad ...(3)$$

$$\frac{(2)}{(1)} \Rightarrow \frac{38.40 \text{ x } 10^{-2}}{19.26 \text{ x } 10^{-2}} = \frac{k\,[1.3]^m[2.2]^n}{k\,[1.3]^m[1.1]^n}$$

$$2 = \left(\frac{2.2}{1.1}\right)^n$$

$$2 = 2^n \quad \text{i.e., } n = 1$$

Therefore the reaction is first order with respect to O_2

$$\frac{(3)}{(1)} \Rightarrow \frac{76.8 \text{ x } 10^{-2}}{19.26 \text{ x } 10^{-2}} = \frac{k\,[2.6]^m[1.1]^n}{k\,[1.3]^m[1.1]^n}$$

$$4 = \left(\frac{2.6}{1.3}\right)^m$$

$$4 = 2^m \quad \text{i.e., } m = 2$$

Therefore the reaction is second order with respect to NO

The rate law is $\text{Rate}_1 = k\,[NO]^2[O_2]^1$

The overall order of the reaction = (2 + 1) = 3

Differences between rate and rate constant of a reaction:

s.no	Rate of a reaction	Rate constant of a reaction
1	It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant

s.no	Rate of a reaction	Rate constant of a reaction
2	It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
3	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

7.4 Molecularity:

Kinetic studies involve not only measurement of a rate of reaction but also proposal of a reasonable reaction mechanism. Each and every single step in a reaction mechanism is called an elementary reaction.

An elementary step is characterized by its molecularity. The total number of reactant species that are involved in an elementary step is called molecularity of that particular step. Let us recall the hydrolysis of t-butyl bromide studied in XI standard. Since the rate determining elementary step involves only t-butyl bromide, the reaction is called a Unimolecular Nucleophilic substitution (S_N^1) reaction.

Let us understand the elementary reactions by considering another reaction, the decomposition of hydrogen peroxide catalysed by I^-.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

It is experimentally found that the reaction is first order with respect to both H_2O_2 and I^-, which indicates that I^- is also involved in the reaction. The mechanism involves the following steps.

Step:1

$$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + OI^-(aq)$$

Step : 2

$$H_2O_2(aq) + OI^-(aq) \rightarrow H_2O(l) + I^-(aq) + O_2(g)$$

Overall reaction is

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

These two reactions are elementary reactions. Adding equ (1) and (2) gives the overall reaction. Step 1 is the rate determining step, since it involves both H_2O_2 and I^-, the overall reaction is bimolecular.

Differences between order and molecularity:

s.no	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
3	It is assigned for a overall reaction.	It is assigned for each elementary step of mechanism.

Example 1

Consider the oxidation of nitric oxide to form NO_2

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

(a). Express the rate of the reaction in terms of changes in the concentration of NO, O_2 and NO_2.

(b). At a particular instant, when $[O_2]$ is decreasing at $0.2\ mol\ L^{-1}s^{-1}$ at what rate is $[NO_2]$ increasing at that instant?

Solution:

a) $$Rate = \frac{-1}{2}\frac{d[NO]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

b) $$\frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = 2x\left(\frac{-d[O_2]}{dt}\right) = 2\ x 0.2\ mol\ L^{-1}s^{-1}$$

$$= 0.4\ mol\ L^{-1}s^{-1}$$

Evaluate yourself 1

1). Write the rate expression for the following reactions, assuming them as elementary reactions.

i) $3A + 5B_2 \longrightarrow 4CD$

ii) $X_2 + Y_2 \longrightarrow 2XY$

2). Consider the decomposition of $N_2O_5(g)$ to form $NO_2(g)$ and $O_2(g)$. At a particular instant N_2O_5 disappears at a rate of $2.5x10^{-2}\ mol\ dm^{-3}s^{-1}$ At what rates are NO_2 and O_2 formed? What is the rate of the reaction?

Example 2

1. What is the order with respect to each of the reactant and overall order of the following reactions?

(a). $$5Br^{-}(aq) + BrO_3^{-}(aq) + 6H^{+}(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$$

The experimental rate law is

$$Rate = k\,[Br^{-}][BrO_3^{-}][H^{+}]^2$$

(b). $$CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)$$

the experimental rate law is

$$Rate = k\,[CH_3CHO]^{\frac{3}{2}}$$

Solution:

a) First order with respect to Br^{-}, first order with respect to BrO_3^{-} and second order with respect to H^{+}. Hence the overall order of the reaction is equal to $1 + 1 + 2 = 4$

b) Order of the reaction with respect to acetaldehyde is $\frac{3}{2}$ and overall order is also $\frac{3}{2}$

Example 3

2. The rate of the reaction $x + 2y \rightarrow product$ is $4\ x\ 10^{-3}\ mol\ L^{-1}s^{-1}$, if $[x]=[y]=0.2\ M$ and rate constant at 400K is $2\ x\ 10^{-2}s^{-1}$, What is the overall order of the reaction.

Solution :

$$Rate = k\,[x]^n[y]^m$$

$$4\ x\ 10^{-3}\ mol\ L^{-1}s^{-1} = 2\ x\ 10^{-2}\ s^{-1}(0.2 mol\ L^{-1})^n(0.2 mol\ L^{-1})^m$$

$$\frac{4\ x\ 10^{-3}\ mol\ L^{-1}s^{-1}}{2\ x\ 10^{-2}\ s^{-1}} = (0.2)^{n+m}\left(mol\ L^{-1}\right)^{n+m}$$

$$0.2\left(mol\ L^{-1}\right) = (0.2)^{n+m}\left(mol\ L^{-1}\right)^{n+m}$$

Comparing the powers on both sides

The overall order of the reaction $n + m = 1$

Evaluate yourself 2

1). For a reaction, $X + Y \longrightarrow product$; quadrupling [x], increases the rate by a factor of 8. Quadrupling both [x] and [y], increases the rate by a factor of 16. Find the order of the reaction with respect to x and y. what is the overall order of the reaction?

2). Find the individual and overall order of the following reaction using the given data.

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Experiment number	Initial concentration		Initial rate
	NO		NOCl mol $L^{-1}s^{-1}$
1	0.1	0.1	7.8×10^{-5}
2	0.2	0.1	3.12×10^{-4}
3	0.2	0.3	9.36×10^{-4}

7.5 The integrated rate equation:

We have just learnt that the rate of change of concentration of the reactant is directly proportional to that of concentration of the reactant. For a general reaction,

$$A \longrightarrow \text{product}$$

The rate law is

$$\text{Rate} = \frac{-d[A]}{dt} = k\,[A]^x$$

Where k is the rate constant, and x is the order of the reaction. The above equation is a differential equation, $\frac{-d[A]}{dt}$, so it gives the rate at any instant. However, using the above expression, we cannot answer questions such as how long will it take for a specific concentration of A to be used up in the reaction? What will be the concentration of reactant after a time ' t '?. To answer such questions, we need the integrated form of the above rate law which contains time as a variable.

7.5.1 Integrated rate law for a first order reaction

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following Cl_2 first order reaction,

$$A \longrightarrow \text{product}$$

Rate law can be expressed as

$$\text{Rate} = k\,[A]^1$$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k\,[A]^1$$

$$\Rightarrow \frac{-d[A]}{[A]} = k\,dt \qquad ...(1)$$

Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration $[A_0]$ to [A] at the later time.

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k\int_0^t dt$$

$$\left(-\ln[A]\right)_{[A_0]}^{[A]} = k\left(t\right)_0^t$$

$$-\ln[A] - \left(-\ln[A_0]\right) = k\,(t-0)$$

$$-\ln[A] + \ln[A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt \qquad ...(2)$$

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$$2.303\log\left(\frac{[A_0]}{[A]}\right) = kt$$

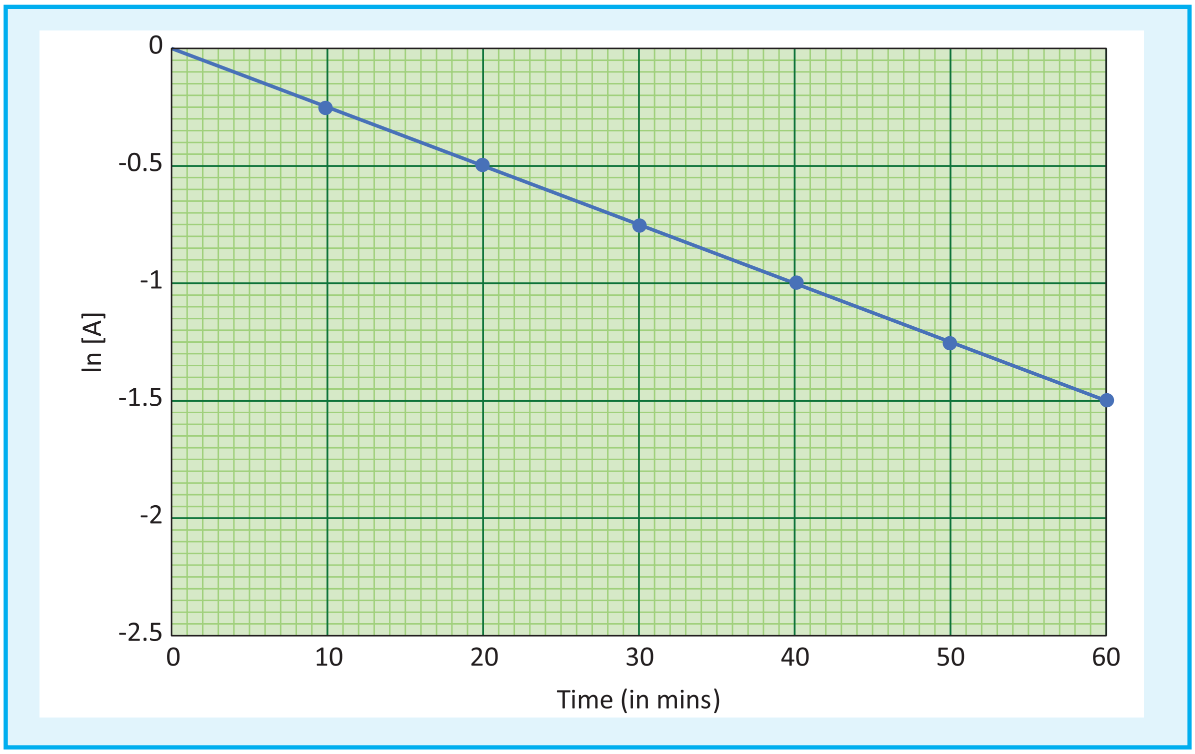


Fig: 7.3 A plot of ln[A] Vs t for a first order reaction, $A \longrightarrow$ product with initial concentration of [A] = 1.00 M and $k = 2.5 \times 10^{-2} \text{min}^{-1}$.

$$k = \frac{2.303}{t} \log\left(\frac{[A_0]}{[A]}\right) \text{ ----- (3)}$$

Equation (2) can be written in the form $y = mx + c$ as below

$$\ln[A_0] - \ln[A] = kt$$

$$\ln[A] = \ln[A_0] - kt$$

$$\Rightarrow y = c + mx$$

If we follow the reaction by measuring the concentration of the reactants at regular time interval't', a plot of ln[A] against 't' yields a straight line with a negative slope.From this, the rate constant is calculated.

Examples for the first order reaction

(i) Decomposition of dinitrogen pentoxide

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

(ii) Decomposition of thionylchloride; $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$

(iii) Decomposition of the H_2O_2 in aqueous solution; $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(iv) Isomerisation of cyclopropane to propene.

Pseudo first order reaction:

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, A second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction. Let us consider the acid hydrolysis of an ester,

$$CH_3COOCH_3\ (aq) + H_2O\ (l) \xrightarrow{H^+} CH_3COOH\ (aq) + CH_3OH\ (aq)$$

$$\text{Rate} = k\,[CH_3COOCH_3]\,[H_2O]$$

If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e.,concentration of water remains almost a constant.

Now, we can define $k\,[H_2O] = k'$; Therefore the above rate equation becomes

$$\text{Rate} = k'\,[CH_3COOCH_3]$$

Thus it follows first order kinetics.

7.5.2 Integrated rate law for a zero order reaction:

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions. Such reactions are rare. Let us consider the following hypothetical zero order reaction.

$A \longrightarrow \text{product}$

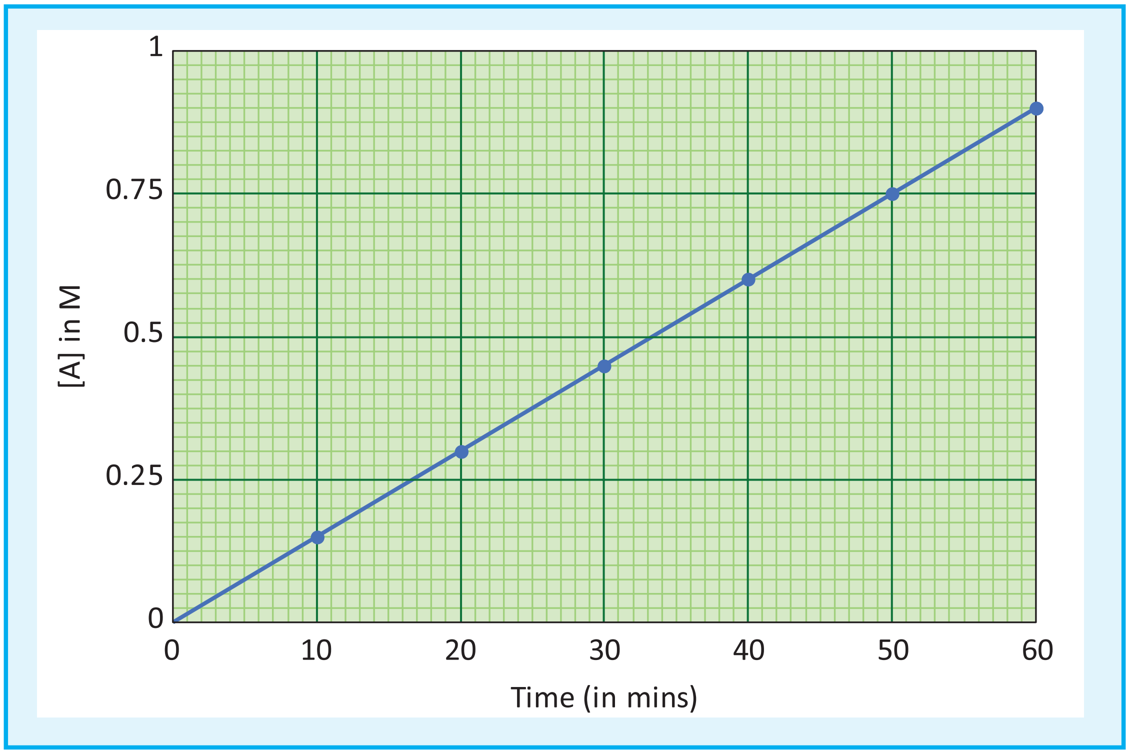


Fig 7.4 : A plot of [A] Vs time for a zero order reaction $A \longrightarrow \text{product}$ with initial concentration of $[A] = 0.5M$ and $k = 1.5\text{x}10^{-2}\text{mol}^{-1}\text{L}^{-1}\text{min}^{-1}$

The rate law can be written as,

$$\text{Rate} = k\,[A]^0$$

$$\frac{-d[A]}{dt} = k\ (1) \qquad \left(\therefore [A]^0 = 1\right)$$

$$\Rightarrow \quad -d[A] = k\,dt$$

Integrate the above equation between the limits of $[A_0]$ at zero time and $[A]$ at some later time 't',

$$-\int_{[A_0]}^{[A]} d[A] = k\int_0^t dt$$

$$-([A])_{[A_0]}^{[A]} = k\,(t)_0^t$$

$$[A_0] - [A] = kt$$

$$k = \frac{[A_0] - [A]}{t}$$

Equation (2) is in the form of a straight line $y = mx + c$

$$\text{Ie., } [A] = -kt + [A_0]$$

$$\Rightarrow y = c + mx$$

A plot of $[A]$ Vs time gives a straight line with a slope of $-k$ and y - intercept of $[A_0]$.

Examples for a zero order reaction:

1. Photochemical reaction between H_2 and I_2

   $$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

2. Decomposition of N_2O on hot platinum surface

   $$N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$$

3. Iodination of acetone in acid medium is zero order with respect to iodine.

   $$CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$$

   $$\text{Rate} = k\,[CH_3COCH_3]\,[H^+]$$

General rate equation for a nth order reaction involving one reactant [A].

$$A \longrightarrow \text{product}$$

$$\text{Rate law } \frac{-d[A]}{dt} = k[A]^n$$

Consider the case in which n≠1, integration of above equation between $[A_0]$ and $[A]$ at time $t = 0$ and $t = t$ respectively gives $\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}} = (n-1)kt$

7.6 Half life period of a reaction:

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant i.e., it does not depend on the initial concentration.

The rate constant for a first order reaction is given by

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$\text{at } t = t_{1/2}\ ;\ [A] = [A_0]/2$$

$$k = \frac{2.303}{t_{1/2}}\log\frac{[A_0]}{[A_0]/2}$$

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

$$k = \frac{2.303 \times 0.3010}{t_{1/2}} = \frac{0.6932}{t_{1/2}}$$

$$t_{1/2} = \frac{0.6932}{k}$$

Let us calculate the half life period for a zero order reaction.

Rate constant, $k = \frac{[A_0]-[A]}{t}$

at $t = t_{1/2}$; $[A] = [A_0]/2$

$$k = \frac{[A_0] - [A_0]/2}{t_{1/2}}$$

$$k = \frac{[A_0]}{2t_{1/2}}$$

$$t_{1/2} = \frac{[A_0]}{2k}$$

Hence, in contrast to the half life of a first order reaction, the half life of a zero order reaction is directly proportional to the initial concentration of the reactant.

More to know

Half life for an nth order reaction involving reactant A and $n \neq 1$

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k\,[A_0]^{n-1}}$$

Example 4

(i) A first order reaction takes 8 hours for 90% completion. Calculate the time required for 80% completion. (log 5 = 0.6989 ; log10 = 1)

Solution:

For a first order reaction,

$$k = \frac{2.303}{t}\log\left(\frac{[A_0]}{[A]}\right) \qquad \text{....(1)}$$

Let $[A_0] = 100M$

When

$t = t_{90\%}$; $[A]=10M$ (given that $t_{90\%}$ =8hours)

$t = t_{80\%}$; $[A]=20M$

$$k = \frac{2.303}{t_{80\%}}\log\left(\frac{100}{20}\right)$$

$$t_{80\%} = \frac{2.303}{k}\log(5) \text{———}(2)$$

Find the value of k using the given data

$$k = \frac{2.303}{t_{90\%}}\log\left(\frac{100}{10}\right)$$

$$k = \frac{2.303}{8 \text{ hours}}\log 10$$

$$k = \frac{2.303}{8 \text{ hours}}(1)$$

Substitute the value of k in equation (2)

$$t_{80\%} = \frac{2.303}{2.303/8 \text{ hours}}\log(5)$$

$t_{80\%}$ = 8hours x 0.6989

$t_{80\%}$ = 5.59hours

Example 5

(ii) The half life of a first order reaction $x \longrightarrow$ products is 6.932×10^4s at 500K . What percentage of x would be decomposed on heating at 500K for 100 min. ($e^{0.06} = 1.06$)

Solution:

Given $t_{1/2} = 0.6932 \times 10^4\,s$

To solve : when t=100 min,

$$\frac{[A_0]-[A]}{[A_0]} \times 100 = ?$$

We know that

For a first order reaction, $t_{1/2} = \frac{0.6932}{k}$

$$k = \frac{0.6932}{6.932 \times 10^4}$$

$$k = 10^{-5}\,s^{-1}$$

$$k = \left(\frac{1}{t}\right) \ln\left(\frac{[A_0]}{[A]}\right)$$

$$10^{-5}\,s^{-1} \text{ x } 100 \text{ x } 60 \text{ s} = \ln\left(\frac{[A_0]}{[A]}\right)$$

$$0.06 = \ln\left(\frac{[A_0]}{[A]}\right)$$

$$\frac{[A_0]}{[A]} = e^{0.06}$$

$$\frac{[A_0]}{[A]} = 1.06$$

$$\therefore \frac{[A_0]-[A]}{[A_0]} \times 100\ \%$$

$$= \left(1-\frac{[A]}{[A_0]}\right) \times 100\ \%$$

$$= \left(1-\frac{1}{1.06}\right) \times 100\ \%$$

$$= 5.6\ \%$$

Example 6

Show that in case of first order reaction, the time required for 99.9% completion is nearly ten times the time required for half completion of the reaction.

Let

$[A_0] = 100;$

when $t = t_{99.9\%}$; $[A] = (100-99.9) = 0.1$

$$k = \frac{2.303}{t} \log\left(\frac{[A_0]}{[A]}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log\left(\frac{100}{0.1}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log 1000$$

$$t_{99.9\%} = \frac{2.303}{k} (3)$$

$$t_{99.9\%} = \frac{6.909}{k}$$

$$t_{99.9\%} \simeq 10 \text{ x} \frac{0.69}{k}$$

$$t_{99.9\%} \simeq 10\, t_{1/2}$$

Evaluate yourself:

(1) In a first order reaction $A \longrightarrow products$ 60% of the given sample of A decomposes in 40 min. what is the half life of the reaction?

(2) The rate constant for a first order reaction is $2.3 \text{ X } 10^{-4}\, s^{-1}$ If the initial concentration of the reactant is 0.01M . What concentration will remain after 1 hour?

(3) Hydrolysis of an ester in an aqueous solution was studied by titrating the liberated carboxylic acid against sodium hydroxide solution. The concentrations of the ester at different time intervals are given below.

Time (min)	0	30	60	90
Ester concentration mol L^{-1}	0.85	0.80	0.754	0.71

Show that, the reaction follows first order kinetics.

7.7 Collision theory :

Collision Theory was proposed independently by Max Trautz in 1916 and William Lewis in 1918. This theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules. Let us understand this theory by considering the following reaction.

$$A_2(g) + B_2(g) \longrightarrow 2AB(g)$$

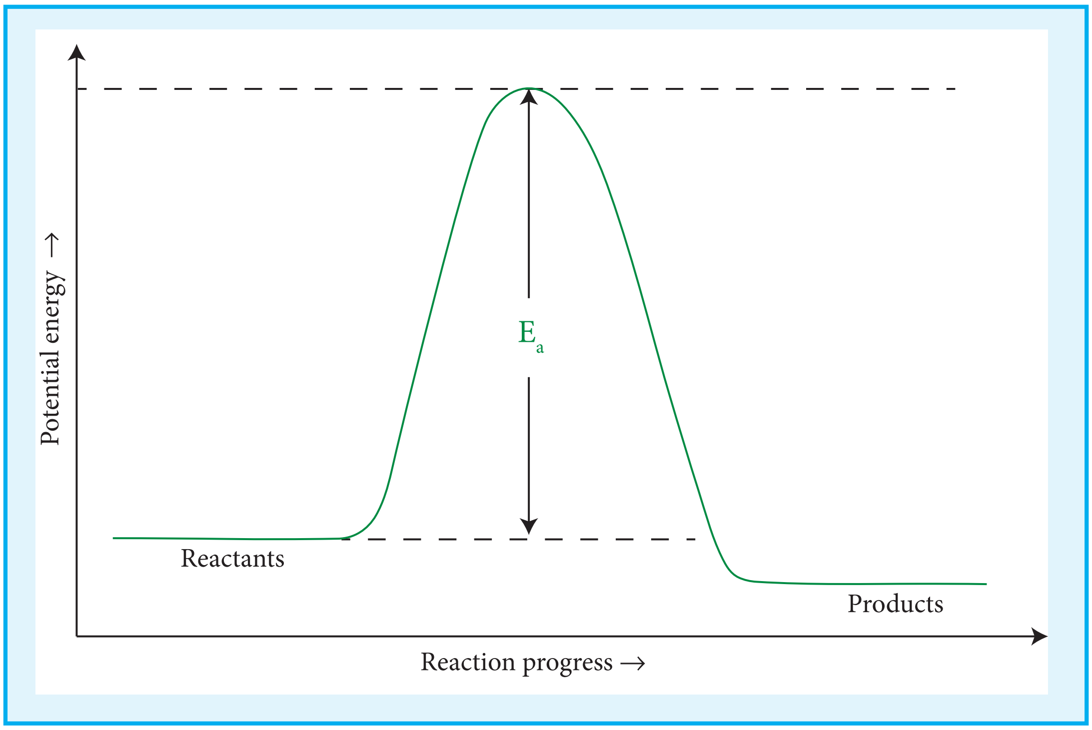


Fig 7.5 progress of the reaction

If we consider that, the reaction between A_2 and B_2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate ∝ number of molecules colliding per litre per second (collision rate)

The number of collisions is directly proportional to the concentration of both A_2 and B_2.

$$\text{Collision rate} \propto [A_2][B_2]$$

$$\text{Collision rate} = Z\,[A_2][B_2]$$

Where, Z is a constant.

The collision rate in gases can be calculated from kinetic theory of gases. For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately 10^9 collisions per second, i.e., 1 collision in 10^{-9} second. Thus, if every collision resulted in reaction, the reaction would be complete in 10^{-9} second. In actual practice this does not happen. It implies that all collisions are not effective to lead to the reaction. In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

Fraction of effective collisions (f) is given by the following expression

$$f = e^{\frac{-E_a}{RT}}$$

To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of $100\ \text{kJ mol}^{-1}$ at 300K.

$$f = e^{-\left(\frac{100 \times 10^3\ \text{J mol}^{-1}}{8.314\text{J K}^{-1}\ \text{mol}^{-1} \times 300K}\right)}$$

$$f = e^{-40} \approx 4 \text{ x } 10^{-18}$$

Thus, out of 10^{18} collisions only four collisions are sufficiently energetic to convert reactants to products. This fraction of collisions is further reduced due to

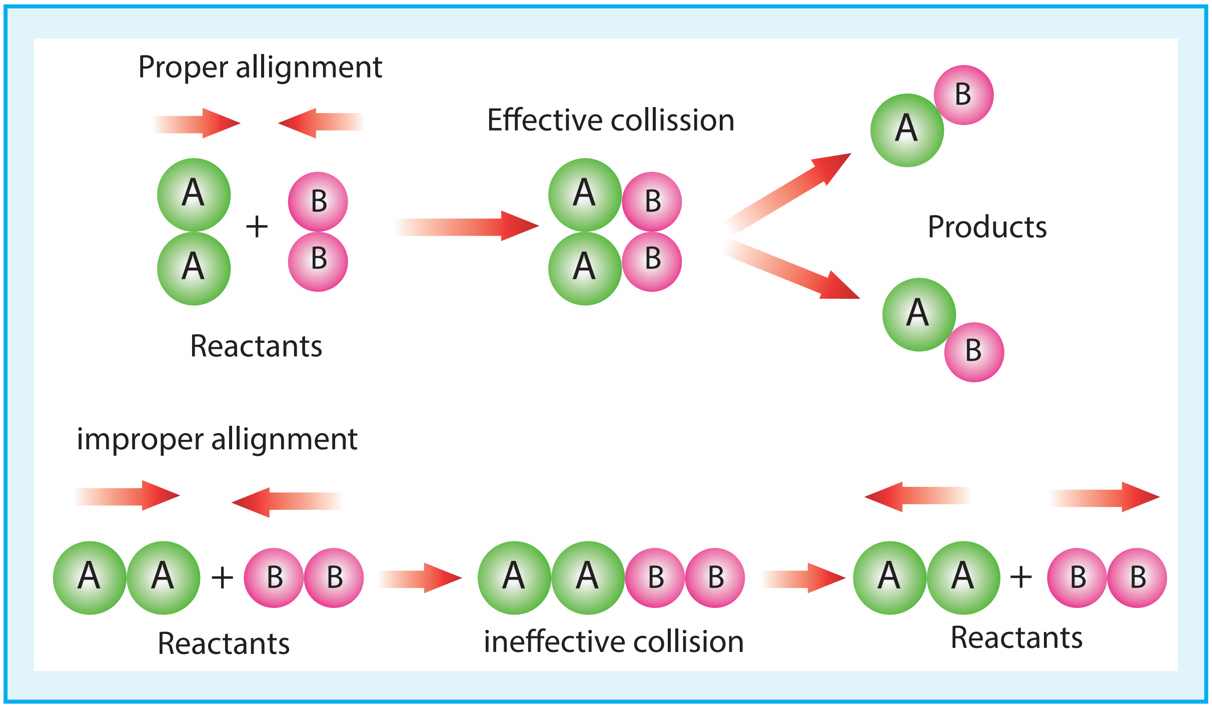


Fig 7.6 - Orientation of reactants - schematic representation

orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.

The figure 7.6 illustrates the importance of proper alignment of molecules which leads to reaction.

The fraction of effective collisions (f) having proper orientation is given by the steric factor p.

$\Rightarrow$ Rate = p x f x collision rate

i.e., $\text{Rate} = p \text{ x } e^{\frac{-E_a}{RT}} \text{ x } Z\, [A_2][B_2]$ ...(1)

As per the rate law,

Rate = k $[A_2]$ $[B_2]$ ...(2)

Where k is the rate constant

On comparing equation (1) and (2), the rate constant k is ‘

$$k = p\,Z\,e^{\frac{-Ea}{RT}}$$

7.8 Arrhenius equation – The effect of temperature on reaction rate

Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10^0C .

Activity

Let us understand the effect of temperature on reaction rate by doing this activity.

i. Take two test tubes, label them as A and B

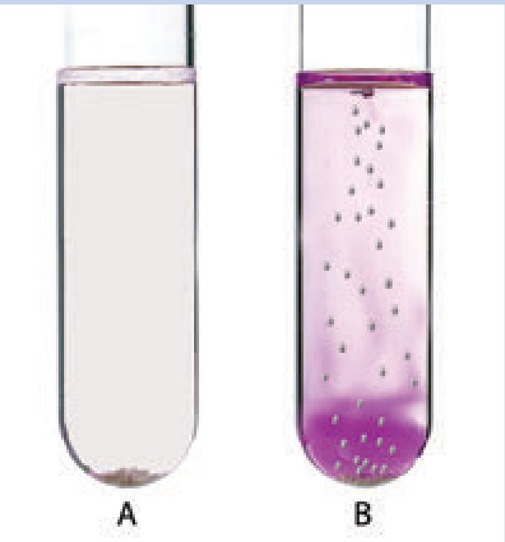
ii. Take 5 ml of cold water in A, add a drop of phenolphthalein indicator and then add Magnesium granules.

iii. Repeat the above with 5 ml of hot water in test tube B.

iv. Observe the two test tubes.

v. The observation shows that the solution in test tube B changes to pink colour and there is no such colour change in test tube A. That is, hot water reacts with magnesium according to the following reaction and there is no such reaction in cold water.

$$Mg + 2H_2O \longrightarrow Mg^{2+} + 2OH^- + H_2\uparrow$$



vi. The resultant solution is basic and it is indicated by phenolphthalein.

A large number of reactions are known which do not take place at room temperature but occur readily at higher temperatures. Example: Reaction between H_2 and O_2 to form H_2O takes place only when an electric spark is passed.

Arrhenius suggested that the rates of most reactions vary with temperature in such a way that the rate constant is directly proportional to $e^{-\left(\frac{E_a}{RT}\right)}$ and he proposed a relation between the rate constant and temperature.

$$k=Ae^{-\left(\frac{E_a}{RT}\right)} \qquad ....(1)$$

Where A the frequency factor,

R the gas constant,

E_a the activation energy of the reaction and,

T the absolute temperature (in K)

The frequency factor (A) is related to the frequency of collisions (number of collisions per second) between the reactant molecules. The factor A does not vary significantly with temperature and hence it may be taken as a constant.

E_a is the activation energy of the reaction, which Arrhenius considered as the minimum energy that a molecule must have to posses to react.

Taking logarithm on both side of the equation (1)

$$\ln k = \ln A + \ln e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \qquad (\therefore\ \ln e = 1)$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad ....(2)$$

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

The above equation is of the form of a straight line y = mx + c.

A plot of $\ln k$ Vs $1/T$ gives a straight line with a negative slope $-\frac{E_a}{R}$. If the rate constant for a reaction at two different temperatures is known, we can calculate the activation energy as follows.

At temperature $T = T_1$; the rate constant $k = k_1$

$$\ln k_1 = \ln A - \left(\frac{E_a}{RT_1}\right) \qquad ....(3)$$

At temperature $T = T_2$; the rate constant $k = k_2$

$$\ln k_2 = \ln A - \left(\frac{E_a}{RT_2}\right) \qquad ....(4)$$

(4) –(3)

$$\ln k_2 - \ln k_1 = -\left(\frac{E_a}{RT_2}\right) + \left(\frac{E_a}{RT_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$2.303\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\ln k_2 - \ln k_1 = -\left(\frac{E_a}{RT_2}\right) + \left(\frac{E_a}{RT_1}\right)$$

This equation can be used to calculate E_a from rate constants k_1 and k_2 at temperatures T_1 and T_2.

Example 7

The rate constant of a reaction at 400 and 200K are 0.04 and 0.02 s^{-1} respectively. Calculate the value of activation energy.

Solution

According to Arrhenius equation

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$T_2 = 400K$; $k_2 = 0.04\ s^{-1}$

$T_1 = 200K$; $k_1 = 0.02\ s^{-1}$

$$\log\left(\frac{0.04\ s^{-1}}{0.02\ s^{-1}}\right) = \frac{E_a}{2.303 \text{ x } 8.314\ JK^{-1}mol^{-1}}\left(\frac{400K - 200K}{200K \text{ x } 400K}\right)$$

$$\log(2) = \frac{E_a}{2.303 \text{ x } 8.314\ JK^{-1}mol^{-1}}\left(\frac{1}{400K}\right)$$

$E_a = \log(2) \text{ x } 2.303 \text{ x } 8.314\ JK^{-1}mol^{-1} \text{ x } 400K$

$E_a = 2305\ J\ mol^{-1}$

Example 8

Rate constant k of a reaction varies with temperature T according to the following Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

Where E_a is the activation energy. When a graph is plotted for $\log k$ Vs $\frac{1}{T}$ a straight line with a slope of -4000K is obtained. Calculate the activation energy

Solution

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

$y = c + mx$

$$m = -\frac{E_a}{2.303R}$$

$E_a = -2.303\ R\ m$

$E_a = -2.303 \text{ x } 8.314\ J\ K^{-1}\ mol^{-1} \text{ x } (-4000K)$

$E_a = 76{,}589 J\ mol^{-1}$

$E_a = 76.589\ kJ\ mol^{-1}$

Evaluate yourself

For a first order reaction the rate constant at 500K is $8 \text{ X } 10^{-4} s^{-1}$. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol^{-1}.

7.9 Factors affecting the reaction rate:

The rate of a reaction is affected by the following factors.

1. Nature and state of the reactant
2. Concentration of the reactant
3. Surface area of the reactant
4. Temperature of the reaction
5. Presence of a catalyst

7.9.1 Nature and state of the reactant:

We know that a chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product. The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

Let us compare the following two reactions that you carried out in volumetric analysis.

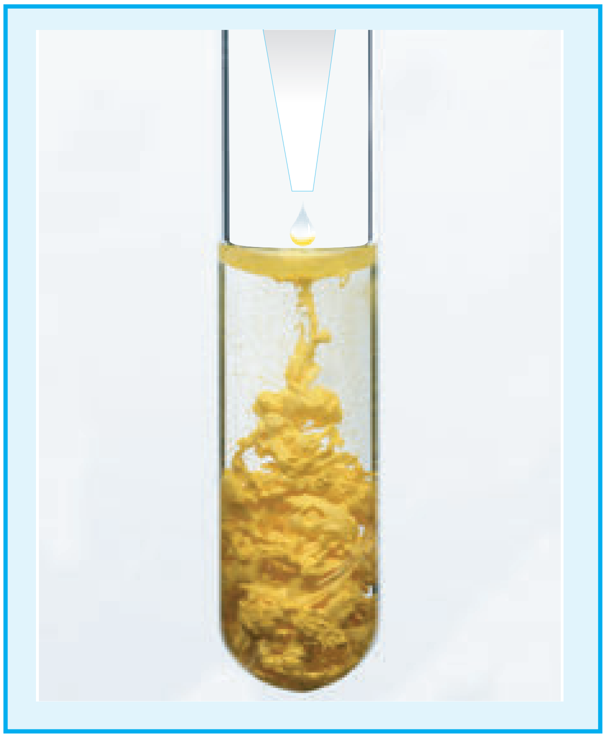
1). Redox reaction between ferrous ammonium sulphate (FAS) and $KMnO_4$

2). Redox reaction between oxalic acid and $KMnO_4$

The oxidation of oxalate ion by $KMnO_4$ is relatively slow compared to the reaction between $KMnO_4$ and Fe^{2+}. In fact heating is required for the reaction between $KMnO_4$ and Oxalate ion and is carried out at around 60^0C.

The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants. For example, reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

Let us consider another example that you carried out in inorganic qualitative analysis of lead salts. If you mix the aqueous solution of colorless potassium iodide with the colorless solution of lead nitrate, precipitation of yellow lead iodide take place instantaneously, whereas if you mix the solid lead nitrate with solid potassium iodide, yellow coloration will appear slowly.



7.9.2 Concentration of the reactants:

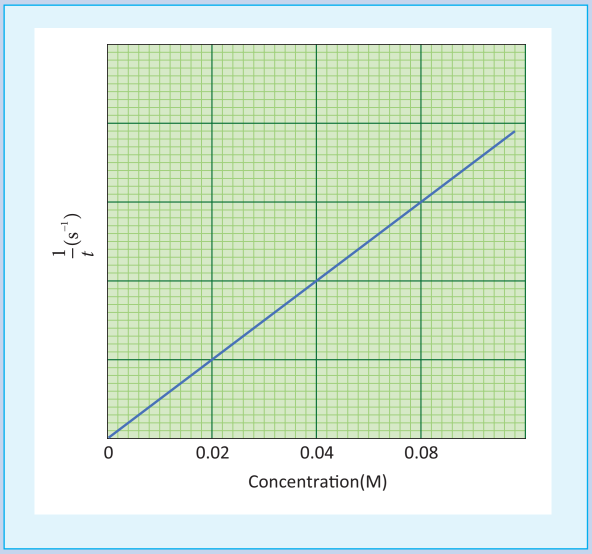
The rate of a reaction increases with the increase in the concentration of the reactants. The effect of concentration is explained on the basis of collision theory of reaction rates. According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules. Higher the concentration, greater is the possibility for collision and hence the rate.

Activity

1. Take three conical flasks and label them as A, B, and C.
2. using a burette, add 10, 20 and 40 ml of 0.1M sodium thiosulphate solution to the flask A, B and C respectively. And then add 40, 30 and 10 ml of distilled water to the respective flasks so that the volume of solution in each flask is 50ml.
3. Add 10 ml of 1M HCl to the conical flask A. Start the stop watch when half of the HCl has been added. Shake the contents carefully and place it on the tile with a cross mark as shown in the figure. Observe the conical flask from top and stop the stops watch when the cross mark just becomes invisible. Note the time.
4. Repeat the experiment with the contents on B and C. Record the observation.

Flask	Volume of $Na_2S_2O_3$	Volume of water	Strength of $Na_2S_2O_3$	Time taken (t)
A	10	40	0.02	
B	20	30	0.04	
C	40	10	0.08	

Draw a graph between $\frac{1}{t}$ Vs concentration of sodium thiosulphate. A graph like the following one is obtained.



$\frac{1}{t}$ is a direct measure of rate of reaction and therefore, the increase in the concentration of reactants i.e $Na_2S_2O_3$, increases the rate.

7.9.3 Effect of surface area of the reactant:

In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate. For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased.For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble

Activity

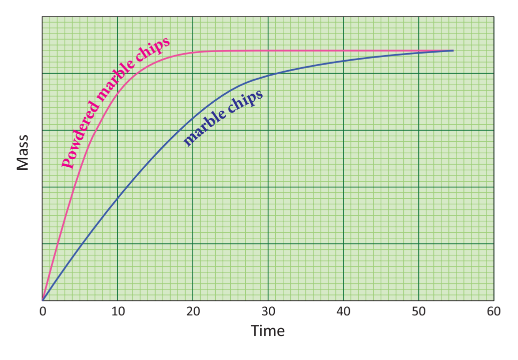
A Known mass of marble chips are taken in a flask and a known volume of dilute HCl is added to the content, a stop clock is started when half the volume of HCl is added. The mass is noted at regular intervals until the reaction is complete. Same experiment is repeated with the same mass of powdered marble chips and the observations are recorded.

Reaction

$$CaCO_3(s) + 2HCl\,(aq) \longrightarrow CaCl_2(aq) + H_2O\,(l) + CO_2(g)$$

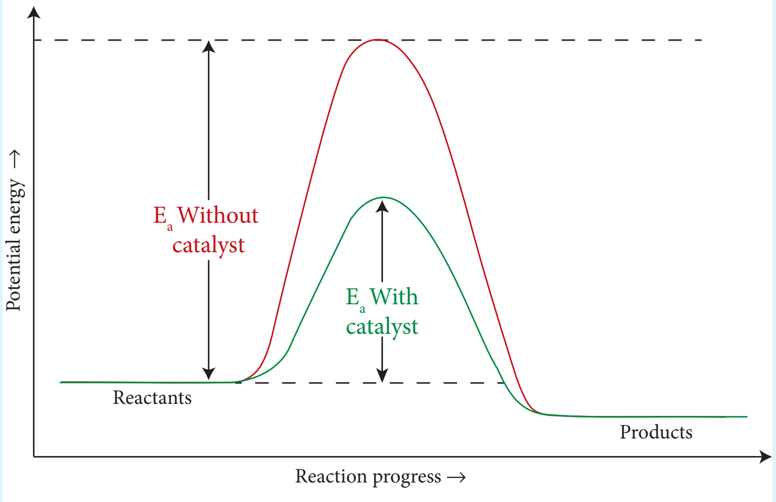
Since, carbon dioxide escapes during reaction, the mass of the flask gets lighter as the reaction proceeds. So, by measuring the flask, we can follow the rate of the reaction. A plot of loss in mass Vs time is drawn and it looks like the one as shown below.

For the powdered marble chips, the reaction is completed in less time. i.e., rate of a reaction increases when the surface area of a solid reactant is increased.



7.9.4 Effect of presence of catalyst:

So far we have learnt, that rate of reaction can be increased to certain extent by increasing the concentration, temperature and surface area of the reactant. However significant changes in the reaction can be brought out by the addition of a substance called catalyst. A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change. They may participate in the reaction, but again regenerated and the end of the reaction. In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.



Activity

Take two test tubes and label them as A and B. Add 7 ml of 0.1N oxalic acid solution, 5 ml of 0.1N $KMnO_4$ solution and 5 ml of 2N dilute H_2SO_4 in both the test tubes. The colour of the solution is pink in both the test tubes.

Now add few crystals of manganese sulphate to the content in test tube A. the pink colour fades up and disappears. In this case, $MnSO_4$ acts as a catalyst and increases the rate of oxidation of $C_2O_4^{2-}$ by MnO_4^-

DO YOU KNOW?

Chemical kinetics in pharmaceuticals

Chemical kinetics has many applications in the field of pharmaceuticals. It is used to study the lifetimes and bioavailability of drugs within the body and this branch of study is called **pharmacokinetics** Doctors usually prescribe drugs to be taken at different times of the day. i.e.some drugs are to be taken twice a day, while others are taken three times a day, or just once a day. Pharmacokinetic studies is used to determine the prescription (dosage and frequency). For example, Paracetamol is a well known anti-pyretic and analgesic that is prescribed in cases of fever and body pain. Pharmacokinetic studies showed that Paracetamol has a half-life of 2.5 hours within the body i.e.the plasma concentration of a drug is halved after 2.5 hrs. After 10 hours (4 half-lives)only 6.25 % of drug remains. Based on such studies the dosage and frequency will be decided. In case of paracetamol, it is usually prescribed to take once in 6 hours depending upon the conditions.

Summary

- Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.
- The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.
- The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,
- The rate represents the speed at which the reactants are converted into products at any instant.
- The rate constant is a proportionality constant and It is equal to the rate of reaction, when the concentration of each of the reactants in unity
- Molecularity of a reaction is the total number of reactant species that are involved in an elementary step.
- The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant

i.e., it does not depend on the initial concentration.

- According to collision theory, chemical reactions occur as a result of collisions between the reacting molecules.
- Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10^0C .
- According to Arrhenius, activation energy of the reaction is the minimum energy that a molecule must have to posses to react.
- The rate of a reaction is affected by the following factors.

1. Nature and state of the reactant
2. Concentration of the reactant
3. Surface area of the reactant
4. Temperature of the reaction
5. Presence of a catalyst

EVALUATION

9G9WX2

1. For a first order reaction $A \longrightarrow B$ the rate constant is $x\ \text{min}^{-1}$. If the initial concentration of A is 0.01M , the concentration of A after one hour is given by the expression.

   a) $0.01\ e^{-x}$ b) $1\times10^{-2}\left(1-e^{-60x}\right)$

   c) $\left(1\times10^{-2}\right)e^{-60x}$ d) none of these

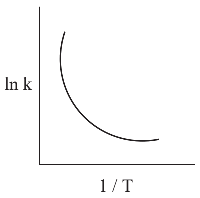
2. A zero order reaction $X \longrightarrow \text{Product}$, with an initial concentration 0.02M has a half life of 10 min. if one starts with concentration 0.04M, then the half life is

   a) 10 s b) 5 min c) 20 min

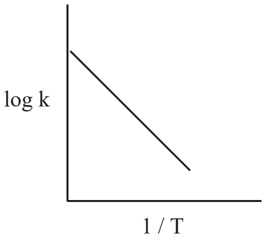
   d) cannot be predicted using the given information

3. Among the following graphs showing variation of rate constant with temperature (T) for a reaction, the one that exhibits Arrhenius behavior over the entire temperature range is

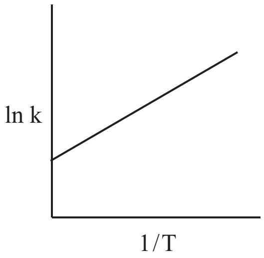
   a)



   b)



   c)



   d) both (b) and (c)

4. For a first order reaction $A \longrightarrow \text{product}$ with initial concentration x mol L^{-1} , has a half life period of 2.5 hours. For the same reaction with initial concentration $\left(\frac{x}{2}\right)$ mol L^{-1} the half life is

a) (2.5×2) hours

b) $\left(\frac{2.5}{2}\right)$ hours

c) 2.5 hours

d) Without knowing the rate constant, $t_{1/2}$ cannot be determined from the given data

5. For the reaction, $2NH_3 \longrightarrow N_2 + 3H_2$, if $\frac{-d[NH_3]}{dt} = k_1[NH_3]$, $\frac{d[N_2]}{dt} = k_2[NH_3]$, $\frac{d[H_2]}{dt} = k_3[NH_3]$

then the relation between k_1, k_2 and k_3 is

a) $k_1 = k_2 = k_3$

b) $k_1 = 3k_2 = 2k_3$

c) $1.5k_1 = 3k_2 = k_3$

d) $2k_1 = k_2 = 3k_3$

6. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the (NEET)

a) rate is proportional to the surface coverage

b) rate is inversely proportional to the surface coverage

c) rate is independent of the surface coverage

d) rate of decomposition is slow

7. For a reaction Rate $= k[\text{acetone}]^{3/2}$ then unit of rate constant and rate of reaction respectively is

a) $(\text{mol L}^{-1}\text{s}^{-1}),(\text{mol}^{-1/2}\ \text{L}^{1/2}\ \text{s}^{-1})$

b) $(\text{mol}^{-1/2}\ \text{L}^{1/2}\ \text{s}^{-1}),(\text{mol L}^{-1}\text{s}^{-1})$

c) $(\text{mol}^{1/2}\ \text{L}^{1/2}\ \text{s}^{-1}),(\text{mol L}^{-1}\text{s}^{-1})$

d) $(\text{mol L s}^{-1}),(\text{mol}^{1/2}\ \text{L}^{1/2}\text{s})$

8. The addition of a catalyst during a chemical reaction alters which of the following quantities? (NEET)

a) Enthalpy
b) Activation energy
c) Entropy
d) Internal energy

9. Consider the following statements :

(i) increase in concentration of the reactant increases the rate of a zero order reaction.

(ii) rate constant k is equal to collision frequency A if $E_a = 0$

(iii) rate constant k is equal to collision frequency A if $E_a = ^\circ$

(iv) a plot of $\ln(k)$ vs T is a straight line.

(v) a plot of $\ln(k)$ vs $\left(\frac{1}{T}\right)$ is a straight line with a positive slope.

Correct statements are

a) (ii) only
b) (ii) and (iv)
c) (ii) and (v)
d) (i), (ii) and (v)

10. In a reversible reaction, the enthalpy change and the activation energy in the forward direction are respectively $-x$ kJ mol^{-1} and y kJ mol^{-1}. Therefore , the energy of activation in the backward direction is

a) $(y - x)$ kJ mol^{-1}

b) $(x + y)$ J mol^{-1}

c) $(x - y)$ kJ mol^{-1}

d) $(x + y) \times 10^3$ J mol^{-1}

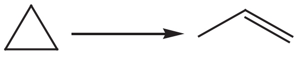
11. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 200K to 400K? (R = 8.314 JK^{-1}mol^{-1})

a) 234.65 kJ mol^{-1}K^{-1}

b) 434.65 kJ mol^{-1}K^{-1}

c) 434.65 J mol^{-1}K^{-1}

d) 334.65 J mol^{-1}K^{-1}

12.  ; This reaction follows first order kinetics. The rate constant at particular temperature is 2.303×10^{-2} hour^{-1}. The initial concentration of cyclopropane is 0.25 M. What will be the concentration of cyclopropane after 1806 minutes? $(\log 2 = 0.3010)$

a) 0.125M b) 0.215M

c) 0.25×2.303M d) 0.05M

13. For a first order reaction, the rate constant is 6.909 min^{-1}.the time taken for 75% conversion in minutes is

a) $\left(\frac{3}{2}\right)\log 2$ b) $\left(\frac{2}{3}\right)\log 2$

c) $\left(\frac{3}{2}\right)\log\left(\frac{3}{4}\right)$ d) $\left(\frac{2}{3}\right)\log\left(\frac{4}{3}\right)$

14. In a first order reaction $x \longrightarrow y$; if k is the rate constant and the initial concentration of the reactant x is 0.1M, then, the half life is

a) $\left(\frac{\log 2}{k}\right)$ b) $\left(\frac{0.693}{(0.1)\,k}\right)$

c) $\left(\frac{\ln 2}{k}\right)$ d) none of these

15. Predict the rate law of the following reaction based on the data given below

$$2A + B \longrightarrow C + 3D$$

Reaction number	[A] (min)	[B] (min)	Initial rate (M s^{-1})
1	0.1	0.1	x
2	0.2	0.1	$2x$
3	0.1	0.2	$4x$
4	0.2	0.2	$8x$

a) $\text{rate} = k[A]^2[B]$ b) $\text{rate} = k[A][B]^2$

c) $\text{rate} = k[A][B]$

d) $\text{rate} = k[A]^{1/2}[B]^{3/2}$

16. Assertion: rate of reaction doubles when the concentration of the reactant is doubles if it is a first order reaction.

Reason: rate constant also doubles

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false.

17. The rate constant of a reaction is 5.8×10^{-2} s^{-1}. The order of the reaction is

a) First order b) zero order

c) Second order d) Third order

18. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the value of rate of disappearance of N_2O_5 is given as 6.5×10^{-2} mol L^{-1}s^{-1}. The rate of formation of NO_2 and O_2 is given

respectively as

a) $\left(3.25\times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\right)$ and $\left(1.3\times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\right)$

b) $\left(1.3\times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\right)$ and $\left(3.25\times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\right)$

c) $\left(1.3\times 10^{-1}\ \text{mol L}^{-1}\text{s}^{-1}\right)$ and $\left(3.25\times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\right)$

d) None of these

19. During the decomposition of H_2O_2 to give dioxygen, 48 g O_2 is formed per minute at certain point of time. The rate of formation of water at this point is

a) 0.75 mol min^{-1}

b) 1.5 mol min^{-1}

c) 2.25 mol min^{-1}

d) 3.0 mol min^{-1}

20. If the initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is

a) Zero
b) one
c) Fraction
d) none

21. In a homogeneous reaction $A \longrightarrow B + C + D$, the initial pressure was P_0 and after time t it was P. expression for rate constant in terms of P_0, P and t will be

a) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0 - P}\right)$

b) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{P_0 - P}\right)$

c) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{3P_0 - P}{2P_0}\right)$

d) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0 - 2P}\right)$

22. If 75% of a first order reaction was completed in 60 minutes , 50% of the same reaction under the same conditions would be completed in

a) 20 minutes
b) 30 minutes
c) 35 minutes
d) 75 minutes

23. The half life period of a radioactive element is 140 days. After 560 days , 1 g of element will be reduced to

a) $\left(\frac{1}{2}\right)g$
b) $\left(\frac{1}{4}\right)g$
c) $\left(\frac{1}{8}\right)g$
d) $\left(\frac{1}{16}\right)g$

24. The correct difference between first and second order reactions is that (NEET)

a) A first order reaction can be catalysed; a second order reaction cannot be catalysed.

b) The half life of a first order reaction does not depend on $[A_0]$; the half life of a second order reaction does depend on $[A_0]$.

c) The rate of a first order reaction does not depend on reactant concentrations; the rate of a second order reaction does depend on reactant concentrations.

d) The rate of a first order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations.

25. After 2 hours, a radioactive substance becomes $\left(\frac{1}{16}\right)^{th}$ of original amount.

Then the half life (in min) is

a) 60 minutes b) 120 minutes

c) 30 minutes d) 15 minutes

Answer the following questions:

1. Define average rate and instantaneous rate.
2. Define rate law and rate constant.
3. Derive integrated rate law for a zero order reaction $A \longrightarrow \text{product}$.
4. Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.
5. What is an elementary reaction? Give the differences between order and molecularity of a reaction.
6. Explain the rate determining step with an example.
7. Describe the graphical representation of first order reaction.
8. Write the rate law for the following reactions.
   - (a) A reaction that is 3/2 order in x and zero order in y.
   - (b) A reaction that is second order in NO and first order in Br_2.
9. Explain the effect of catalyst on reaction rate with an example.
10. The rate law for a reaction of A, B and C has been found to be $\text{rate} = k[A]^2[B][L]^{3/2}$. How would the rate of reaction change when
    - (i) Concentration of [L] is quadrupled
    - (ii) Concentration of both [A] and [B] are doubled
    - (iii) Concentration of [A] is halved
    - (iv) Concentration of [A] is reduced to $\left(1/3\right)$ and concentration of [L] is quadrupled.
11. The rate of formation of a dimer in a second order reaction is 7.5×10^{-3} mol $L^{-1} s^{-1}$ at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant.
12. For a reaction $x + y + z \longrightarrow \text{products}$ the rate law is given by $\text{rate} = k[x]^{3/2}[y]^{1/2}$ what is the overall order of the reaction and what is the order of the reaction with respect to z.
13. Explain briefly the collision theory of bimolecular reactions.
14. Write Arrhenius equation and explains the terms involved.
15. The decomposition of Cl_2O_7 at 500K in the gas phase to Cl_2 and O_2 is a first order reaction. After 1 minute at 500K, the pressure of Cl_2O_7 falls from 0.08 to 0.04 atm. Calculate the rate constant in s^{-1}.
16. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of an ester at different temperatures is given below.
17. Explain pseudo first order reaction with an example.
18. Identify the order for the following reactions

(i) Rusting of Iron

(ii) Radioactive disintegration of ${}_{92}U^{238}$

(iii) $2A + 3B \longrightarrow \text{products}\,;\ \text{rate} = k[A]^{1/2}[B]^2$

19. A gas phase reaction has energy of activation 200 kJ mol^{-1}. If the frequency factor of the reaction is $1.6 \times 10^{13}\ s^{-1}$

. Calculate the rate constant at 600 K. $\left(e^{-40.09} = 3.8\times10^{-18}\right)$

20. For the reaction $2x + y \longrightarrow L$ find the rate law from the following data.

[x] (min)	[y] (min)	rate (M s^{-1})
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

21. How do concentrations of the reactant influence the rate of reaction?

22. How do nature of the reactant influence rate of reaction.

23. The rate constant for a first order reaction is $1.54\times10^{-3}\,s^{-1}$. Calculate its half life time.

24. The half life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?

25. The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds?

26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

27. The activation energy of a reaction is 225 k Cal mol^{-1} and the value of rate constant at 40°C is $1.8\times10^{-5}\ s^{-1}$. Calculate the frequency factor, A.

28. Benzene diazonium chloride in aqueous solution decomposes according to the equation $C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$. Starting with an initial concentration of 10 g L^{-1}, the volume of N_2 gas obtained at 50 °C at different intervals of time was found to be as under:

t (min):	6	12	18	24	30	∞
Vol. of N_2 (ml):	19.3	32.6	41.3	46.5	50.4	58.3

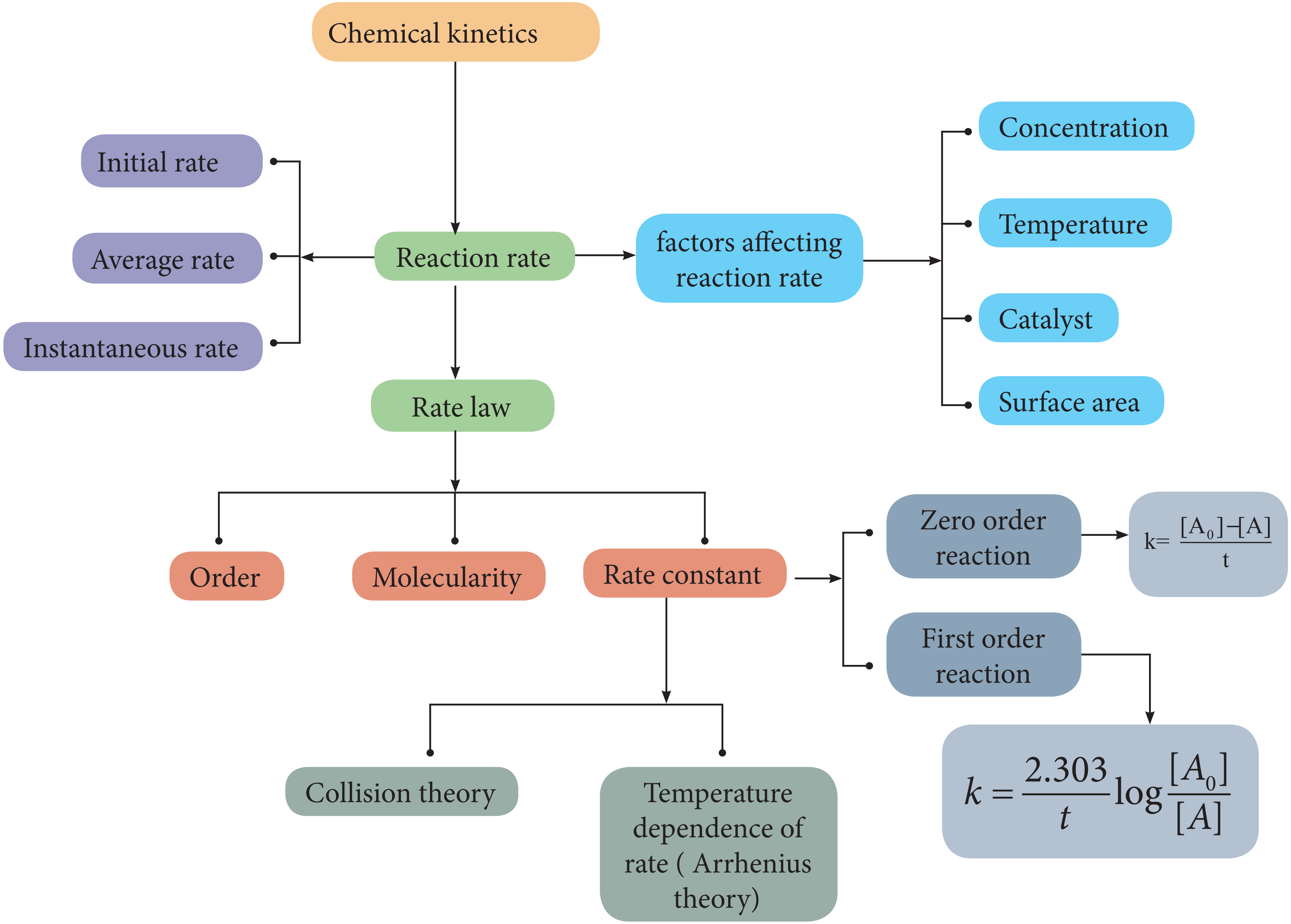
Show that the above reaction follows the first order kinetics. What is the value of the rate constant?

29. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order:

t (min)	0	10	20
V (ml)	46.1	29.8	19.3

Where *t* is the time in minutes and V is the volume of standard $KMnO_4$ solution required for titrating the same volume of the reaction mixture.

30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?


Chemical kinetics
Reaction rate
Initial rate
Average rate
Instantaneous rate
factors affecting reaction rate
Concentration
Temperature
Catalyst
Surface area
Rate law
Order
Molecularity
Rate constant
Zero order reaction
$k=\frac{[A_0]-[A]}{t}$
First order reaction
$k=\frac{2.303}{t}\log\frac{[A_0]}{[A]}$
Collision theory
Temperature dependence of rate (Arrhenius theory)

ICT Corner

CHEMICAL KINETICS

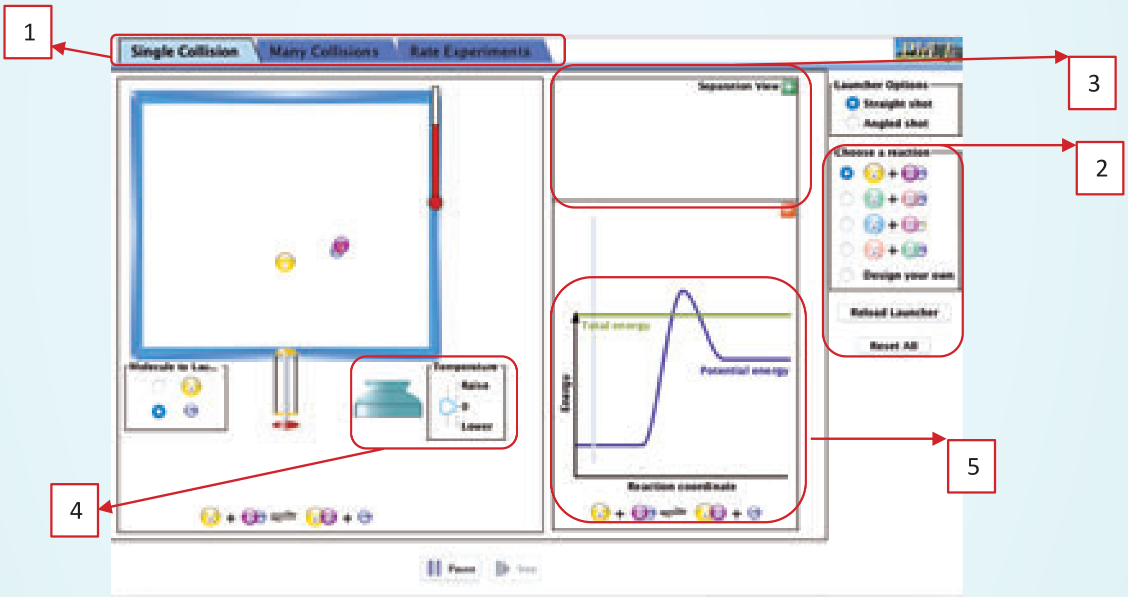
By using this tool you can understand collision and the activation energy. You can also perform virtual kinetic experiment to understand the effect of temperature on reaction rate.

Please go to the URL https://phet.colorado.edu/en/simulation/legacy/reactions-and-rates
(or) Scan the QR code on the right side

B264_12_CHEMISTRY_EM

Steps

- Open the Browser and type the URL given (or) Scan the QR Code. You can see a webpage which displays the java applet called reactions and rates. You can click it and you will get a window as shown in the figure. This applet contains three modules which can be selected by clicking the appropriate tab (box1).
- Select single collision tab (tab 1) to visualise collision between two molecules. You can visualise the progress of the reaction (box 5) by varying the temperature using the slider (box 2). You can visualise that the raise in temperature, will raise the energy of the system and allows the reactants to cross the energy barrier to form products. You can repeat this simulation with more molecules in the many collisions tab (box 1).
- You can also perform virtual kinetic experiment, using rate experiments mode. Choose the types reacting molecules and their stoichiometry using the options provided (box 2). The number of reactant and product molecules at a given time will be displayed in panel (box-3). You can see the effect of temperature on reaction rate by varying the temperature (box 4).



VOLUME I

ANSWERS

UNIT-I

Choose the correct answer

1. b) $Al_2O_3.nH_2O$

2. c) SO_2

3. c) $MgCO_3 \longrightarrow MgO + CO_2$

4. b) Al_2O_3

5. a) Al

6. d) Carbon and hydrogen are suitable reducing agents for metal sulphides.

7. c) A-iv , B-ii , C-iii , D-i

8. d)Electromagnetic separation

9. b) $Cu(s) + Zn^{2+}(aq) \longrightarrow Zn(s) + Cu^{2+}(aq)$

10. c) sodium

11. b) Infusible impurities to soluble impurities

12. c) Galena

13. a) Lower the melting point of alumina

14. a) Carbon reduction

15. a) Silver

16. c) Displacement with zinc

17. c) Mg

18. b) van Arkel process

19. d) Both (a) and (c)

20. d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution

21. b) Impure copper

22. b) ΔG^0 Vs T

23. c) $\left(\frac{\Delta G^0}{\Delta T}\right)$ is negative

24. b) $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al$

25. b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.

UNIT-2

Choose the correct answer:

1. c) basic

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

2. d) accepts OH^- from water ,releasing proton.

$$B(OH)_3 + H_2O \rightleftharpoons \left[B(OH)_4\right]^- + H^+$$

3. b) B_3H_6

nido borane : B_nH_{4+n}

aracno borane : B_nH_{6+n}

B_3H_6 is not a borane

4. a) Aluminium

5. c) four

There are two 3c – $2e^-$ bonds i.e., the bonding in the bridges account for 4 electrons.

6. c) Lead

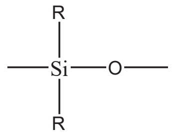
7. c) sp^2 hybridised

8. a) +4

Example : CH_{4+} in which the oxidation state of carbon is +4

9. d) $(SiO_4)^{4-}$

10. b)



11. a) Me_3SiCl

12. d) dry ice

dry ice – solid CO_2 in which carbon is in sp hybridized state

13. a) Tetrahedral

14. d) Feldspar is a three dimensional silicate

15. b) $K_3[AlF_6]$

$$AlF_3 + 3KF \longrightarrow K_3[AlF_6]$$

16. a) A-b , B-1 , C-4 , D-3

17. d) Al,Cu,Mn,Mg

Al-95% , Cu-4% , Mn-0.5% , Mn-0.5%

18. b) graphite

19. a) Metal borides

20. a) Al < Ga < In < Tl

stability of +1 oxidation state decreases down the group due to inert pair effect

UNIT-3

Choose the correct answer:

1. a) Nessler's reagent

2. d) ability to form $p\pi - p\pi$ bonds with itself

3. d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

4. b) P_4(white) and PH_3

5. b) Nitroso ferrous sulphate

6. a) H_3PO_3

7. a) H_3PO_3

8. b) 2

9. a) 6N

10. d) Both assertion and reason are wrong. The converse is true.

11. b) F_2

12. b) HF > HCl > HBr > HI

13. d) NeF_2

14. c) He

15. c) XeO_3

16. c) SO_4^{2-}

17. a) HI

18. d) $Cl_2 > Br_2 > F_2 > I_2$

19. d) $HClO < HClO_2 < HClO_3 < HClO_4$

20. c) $Cu(NO_3)_2$ and NO_2

UNIT-4

Choose the correct answer:

1. b) in case of Sc, 3d orbital are partially filled but in Zn these are completely filled

2. a) Cr

   $Cr \Rightarrow [Ar]3d^5 4s^1$

3. a) Ti

4. c) Ni^{2+}

5. a) 5.92BM

   $Mn^{2+} \Rightarrow 3d^5$contains 5 unpaired electrons

   n=5 ; ..= $\sqrt{n(n+2)}BM$

   ..= $\sqrt{5(5+2)} = \sqrt{35} = 5.92BM$

6. b) Ti^{4+}

   Ti^{4+} contains no unpaired electrons in d orbital, hence no d-d transition.

7. c) their ability to adopt variable oxidation states

8. a) $VO_2^{+} < Cr_2O_7^{2-} < MnO_4^{-}$

   $\overset{+5}{V}O_2^{+} < \overset{+6}{Cr}_2O_7^{2-} < \overset{+7}{Mn}O_4^{-}$ greater the oxidation state, higher is the oxidising power

9. d) brass

   Brass contains 70% Cu + 30% Zn

10. b) $(NH_4)_2Cr_2O_7$

    $2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + \left(\frac{3}{2}\right)O_2$

    $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_2$

    $KClO_3 \longrightarrow KCl + \left(\frac{3}{2}\right)O_2$

    $Zn(ClO_3)_2 \longrightarrow ZnCl_2 + 3O_2$

11. b) Carbon dioxide

    $5(COO)_2^{2-} + 2MnO_4^{-} + 16H^{+} \longrightarrow 2Mn^{2+} + 10CO_2\uparrow + 8H_2O$

12. b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

13. b) Mn^{2+}

    $MnO_4^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_2O$

14. a) Na_2SO_3 , SO_2 , $Cr_2(SO_4)_3$

$$\underset{(A)}{Na_2S_2O_3} + 2HCl \longrightarrow 2NaCl + \underset{(B)}{SO_2}\uparrow + \underset{\text{yellow ppt}}{S}\downarrow + H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{(C)}{Cr_2(SO_4)_3} + H_2O$$

15. a) BrO_3^-, MnO_2

$$2MnO_4^- + Br^- + H_2O \longrightarrow 2OH^- + 2MnO_2 + BrO_3^-$$

16. c) 3

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

17. c) 0.6

$$\overset{7+}{Mn}O_4^- + \overset{+2}{Fe}\overset{+3}{C_2}O_4 \longrightarrow Mn^{2+} + Fe^{3+} + 2\overset{+4}{C}O_2$$

$5e^-$ acception $\quad$ $3e^-$ release

5 moles of $FeC_2O_4 \equiv$ 3 moles of $KMnO_4$

1 mole of $FeC_2O_4 \equiv \left(\frac{3}{5}\right)$ moles of $KMnO_4$

1 mole of $FeC_2O_4 \equiv$ 0.6 moles of $KMnO_4$

18. a) MnO_2, Cl_2, NCl_3

$$\underset{(A)}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{(B)}{Cl_2}\uparrow + H_2O$$

$$NH_3 + 3Cl_2 \longrightarrow \underset{(C)}{NCl_3} + 3HCl$$

19. c) All the lanthanons are much more reactive than aluminium.

As we move from La to Lu , their metallic behaviour because almost similar to that of aluminium.

20. b) Yb^{2+}

Yb^{2+} - $4f^{14}$ –no unpaired electrons - diamagnetic

21. d) 3

22. a) Both assertion and reason are true and reason is the correct explanation of assertion.

23. c) +4

24. a) Np, Pu ,Am

25. a) $La(OH)_2$ is less basic than $Lu(OH)_3$

UNIT-5

Choose the correct answer:

1. In the complex $\left[M(en)_2(Ox)\right]Cl$ For the central metal ion M^{3+}

The primary valance is $= +3$

The secondary valance $= 6$

sum of primary valance and secondary valance = 3+6 = 9

Answer : option (d)

2. The complex is $\left[M(H_2O)_5 Cl\right]Cl_2$

1000 ml of 1M solution of the complex gives 2 moles of Cl^- ions

1000 ml of 0.01M solution of the complex will give

$$\frac{100\text{ ml} \times 0.01\text{M} \times 2Cl^-}{1000\text{ ml} \times 1\text{M}} = 0.002 \text{ moles of } Cl^- ions$$

Answer : option (b)

3. Molecular formula: $MSO_4Cl.\ 6H_2O$.

Formation of white precipitate with Barium chloride indicates that SO_4^{2-} ions are outside the coordination sphere, and no precipitate with $AgNO_3$ solution indicates that the Cl^- ions are inside the coordination sphere.Since the coordination number of M is 6, Cl^- and 5 H_2O are ligands, remaining 1 H_2O molecular and SO_4^{2-} are in the outer coordination sphere.

Answer : option (c)

4. $\left[\overset{+}{Fe}(H_2O)_5\overset{+}{NO}\right]^{2+} SO_4^{2-}$

+1 and +1 respectively

Answer : option(d)

5. Answer : option(d)

6. Answer : option(d)

7. Answer : option(c)

$Ti^{4+}\left(d^0 \Rightarrow 0BM\right)$

$Co^{2+}\left(d^7\text{spin free} \Rightarrow t_{2g}{}^5, e_g{}^2\ ;\ n = 3\ ;\ \mu = 3.9BM\right)$

$Cu^{2+}\left(d^9\text{Low spin} \Rightarrow t_{2g}{}^6, e_g{}^3\ ;\ n = 1\ ;\ \mu = 1.732BM\right)$

$Ni^{2+}\left(d^8\text{Low spin} \Rightarrow t_{2g}{}^6, e_g{}^2\ ;\ n = 2\ ;\ \mu = 2.44BM\right)$

8. Answer : option(b)

The electronic configuration $t_{2g}{}^3, e_g{}^2$

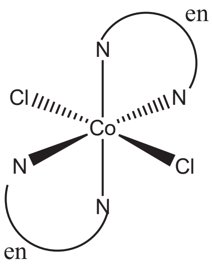
$\left[3\times(-0.4)+2(0.6)\right]\Delta_0$

$[-1.2+1.2]\Delta_0 = 0$

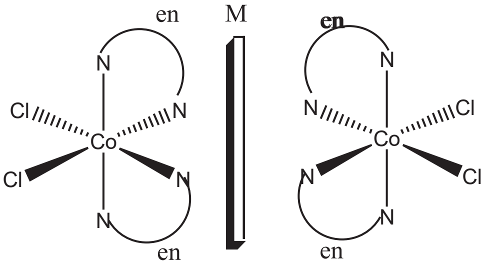
9. Answer : option(a)

In all the complexes, the central metal ion is Co^{3+}, among the given ligands CN^- is the strongest ligand, which causes large crystal field splitting i.e maximum $\varnothing_0$

10. Answer : option(b)



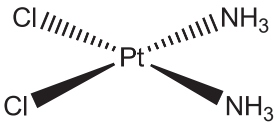
inactive

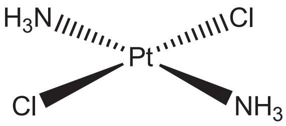


Active forms (enantiomorphs)

Complexes given in other options (a), (c) and (d) have symmetry elements and hence they are optically inactive.

11. Answer : option(d)





12. Three isomers. If we consider any one of the ligands as reference (say Py), the arrangement of other three ligands (NH_3, Br^- and Cl^-) with respect to (Py) gives three geometrical isomers.

13. Answer : option(c)

(a)coordination isomers

(b) no isomerism (different molecular formula)

(c) $\leftarrow NCS$, $\leftarrow SCN$ coordinating atom differs : linkage isomers

14. Answer : option(a)

For $[MA_4B_2]^{n+}$ complexes-geometrical isomerism is possible

$$\left.\begin{cases}[Co(NH_3)_4Br_2]Cl \\ [Co(NH_3)_4Br\,Cl]Br\end{cases}\right\} \rightarrow \text{ionisation isomers}$$

15. Answer : option(d)

Option (a) and (b) – geometrical isomerism is possible

Option (c) – ionization isomerism is possible

Option (d) – no possibility to show either constitutional isomerism or stereo isomerism

16. Answer : option(c)

(a) Fe^{2+} (b) Fe^{3+} (c) Fe^0

17. Answer : option(d)

$$\left[\mathrm{Fe}(\mathrm{en})_3\right]^{2+}\left(\mathrm{PO}_4^{\ 3-}\right)$$

18. Answer : option(c)

(a) $\mathrm{Zn}^{2+}\left(\mathrm{d}^{10} \Rightarrow \text{diamagnetic}\right)$

(b) $\mathrm{Co}^{3+}\left(\mathrm{d}^{6}\text{Low spin} \Rightarrow t_{2g}^{\ 6}, e_g^{\ 0}\ ;\ \text{diamagnetic}\right)$

(c) $\mathrm{Ni}^{2+}\left(\mathrm{d}^{8}\text{Low spin} \Rightarrow t_{2g}^{\ 6}, e_g^{\ 2}\ ;\ \text{paramagnetic}\right)$

(d) $[\mathrm{Ni(CN)}_4]^{2-}\left(\mathrm{dsp}^2\ ;\ \text{square planar, diamagnetic}\right)$

19. Answer : option(c)

$$\left[\mathrm{Co}(\mathrm{NH}_3)_3(Cl)_3\right]$$

20. Answer : option(d)

$\mathrm{V}^{2+}\left(t_{2g}^{\ 3}, e_g^{\ 0}\ ;\ \text{CFSE} = 3 \times (-0.4)\Delta_0 = -1.2\Delta_0\right)$

$\mathrm{Ti}^{2+}\left(t_{2g}^{\ 2}, e_g^{\ 0}\ ;\ \text{CFSE} = 2 \times (-0.4)\Delta_0 = -0.8\Delta_0\right)$

Statements given in option (a) ,(b), and (c) are wrong.

The current statements are

(a) since, the crystal field stabilization is more in octahedral field , octahedral complexes are more stable than square planar complexes.

(b)

$$[\mathrm{FeF}_6]^{4-} - \left(\begin{array}{l}\mathrm{Fe}^{2+} - \mathrm{d}^6\text{High Spin} - t_{2g}^{\ 4}, e_g^{\ 2}\ )\\ \text{CFSE} = 4 \times (-0.4) + (0.6)\times 2 + \mathrm{P}\end{array}\right)$$

$$\left[\mathrm{Fe}(\mathrm{CN})_6\right]^{4-} - \left(\begin{array}{l}\mathrm{Fe}^{2+} - \mathrm{d}^6\ \text{Low Spin} - t_{2g}^{\ 6}, e_g^{\ 0}\ )\\ \text{CFSE} = 6 \times (-0.4) + 3\mathrm{P}\end{array}\right)$$

UNIT-6

Choose the correct answer:

1. c) both covalent crystals

2. b) AB_3

$$\text{number of A ions} = \left(\frac{N_c}{8}\right) = \left(\frac{8}{8}\right) = 1$$

$$\text{number of B ions} = \left(\frac{N_f}{2}\right) = \left(\frac{6}{2}\right) = 3$$

simplest formula AB_3

3. b) 1:2

if number of close packed atoms =N; then,

The number of Tetrahedral holes formed = 2N

number of Octahedral holes formed = N

therefore N:2N = 1:2

4. c) molecular solid

   lattice points are occupied by CO_2 molecules

5. a) Both assertion and reason are true and reason is the correct explanation of assertion.

6. c) 8 and 4

CaF_2 has cubical close packed arrangement

Ca^{2+} ions are in face centered cubic arrangement, each Ca^{2+} ions is surrounded by 8 F^- ions and each F^- ion is surrounded by 4 Ca^{2+} ions.

Therefore coordination number of Ca^{2+} is 8 and of F^- is 4

7. b) 6.023×10^{22}

in bcc unit cell,

2 atoms $\equiv$ 1 unit cell

Number of atoms in 8g of element is ,

$$\text{Number of moles} = \frac{8g}{40\text{ g mol}^{-1}} = 0.2\text{ mol}$$

1 mole contains 6.023×10^{23} atoms

0.2 mole contains $0.2\times6.023\times10^{23}$ atoms

$$\left(\frac{1\text{unit cell}}{2\text{ atoms}}\right)\times0.2\times6.023\times10^{23}$$

6.023×10^{22} unit cells

8. a) 8

   in diamond carbon forming fcc. Carbon occupies corners and face centres and also occupying half of the tetrahedral voids.

$$\left(\frac{N_c}{8}\right)+\left(\frac{N_f}{2}\right)+4\text{ C atoms inTd voids}$$

$$\left(\frac{8}{8}\right)+\left(\frac{6}{2}\right)+4=8$$

9. d) M_3N_2

   if the total number of M atoms is n, then the number of tetrahedral voids =2n

   given that $\left(\frac{1}{3}\right)^{rd}$ of tetrahedral voids are occupied i.e., $\left(\frac{1}{3}\right)\times2n$ are occupied by N atoms

$$\therefore \text{M:N} \Rightarrow n:\left(\frac{2}{3}\right)n$$

$$1:\left(\frac{2}{3}\right)$$

$$3:2 \Rightarrow M_3N_2$$

10. b) 15.05%

    let

    the number of Fe^{2+} ions in the crystal be x

    the number of Fe^{3+} ions in the crystal be y

    total number of Fe^{2+} and Fe^{3+} ions is $x+y$

    given that $x+y=0.93$

    the total charge =0

$$x(2+)+(0.93-x)(+3)-2=0$$

$$2x+2.97-3x-2=0$$

$$x=0.79$$

    Percentage of Fe^{3+}

$$=\left(\frac{(0.93-0.79)}{(0.93)}\right)100=15.05\%$$

11. c) 6

$$\frac{r_{C^+}}{r_{A^-}}=\frac{0.98\times10^{-10}}{1.81\times10^{-10}}=0.54$$

    it is in the range of 0.414 - 0.732, hence the coordination number of each ion is 6

12. d) $\left(\frac{\sqrt{3}}{2}\right)\times400\text{pm}$

$$\sqrt{3}\ a = \mathrm{r}_{Cs^+} + 2\mathrm{r}_{Cl^-} + \ \mathrm{r}_{Cs^+}$$

$$\left(\frac{\sqrt{3}}{2}\right) a = \left(\mathrm{r}_{Cs^+} + \mathrm{r}_{Cl^-}\right)$$

$$\left(\frac{\sqrt{3}}{2}\right) 400 = \text{inter ionic distance}$$

13. a) $\left(\frac{100}{0.414}\right)$

for an fcc structure $\frac{\mathrm{r}_{X^+}}{\mathrm{r}_{y^-}} = 0.414$

given that $\mathrm{r}_{X^+} = 100\,pm$

$$\mathrm{r}_{y^-} = \frac{100\,pm}{0.414}$$

14. c) 32%

packing efficiency = 68%

therefore empty space percentage = (100-68) = 32%

15. b) 848.5pm

let edge length =a

$$\sqrt{2}a = 4r$$

$$a = \frac{4\times\ 300}{\sqrt{2}}$$

$$a = 600\times 1.414$$

$$a = 848.4\ \text{pm}$$

16. b) $\left(\frac{\pi}{6}\right)$

$$\left(\frac{\frac{4}{3}\pi r^3}{a^3}\right) = \left(\frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3}\right) = \left(\frac{\pi}{6}\right)$$

17. a) excitation of electrons in F centers

18. c) $\left(\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a\right)$

$$sc \Rightarrow 2r = a \Rightarrow r = \frac{a}{2}$$

$$bcc \Rightarrow 4r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}a}{4}$$

$$fcc \Rightarrow 4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$$

$$\left(\frac{a}{2}\right) : \left(\frac{\sqrt{3}a}{4}\right) : \left(\frac{a}{2\sqrt{2}}\right)$$

19. d) $\left(\frac{\sqrt{3}}{2}\right)a$

if a is the length of the side, then the length of the leading diagonal passing through the body centered atom is $\sqrt{3}a$

$$\text{Required distance} = \left(\frac{\sqrt{3}}{2}\right)a$$

20. a) 915 kg m-3

$$\rho = \frac{\mathrm{n}\ \times\ \mathrm{M}}{\mathrm{a}^3\mathrm{N}_A}$$

for bcc

$n = 2$

M=39

nearest distance 2r = 4.52

$$a = \frac{4r}{\sqrt{3}} = \frac{2\times 4.52\times 10^{-10}}{\sqrt{3}} = 5.21\times 10^{-10}$$

$$\rho = \frac{2\times 39}{\left(5.21\times 10^{-10}\right)^3 \times \left(6.023\times 10^{23}\right)}$$

$$\rho = 915\ \text{Kg m}^{-3}$$

N_A

21. b) equal number of anions and anions are missing from the lattice

22. c) Frenkel defect

23. d) Both assertion and reason are false

24. b) FeO

25. a) XY_8

UNIT-7

Choose the correct answer:

1. option (c)

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$k = \left(\frac{1}{t}\right)\ln\left(\frac{[A_0]}{[A]}\right)$$

$$e^{kt} = \left(\frac{[A_0]}{[A]}\right)$$

$$[A] = [A_0]e^{-kt}$$

In this case

$k = x\,\text{min}^{-1}$ and $[A_0] = 0.01\text{M} = 1 \times 10^{-2}\text{M}$

t = 1 hour = 60 min

$$[A] = 1 \times 10^{-2}\left(e^{-60x}\right)$$

2. option (c)

for $n \neq 1$ $\quad t_{1/2} = \dfrac{2^{n-1}-1}{(n-1)\,k\,[A_0]^{n-1}}$

for $n = 0$ $\quad t_{1/2} = \dfrac{1}{2\,k\,[A_0]^{-1}}$

$$t_{1/2} = \frac{[A_0]}{2\,k}$$

$$t_{1/2} \propto [A_0] \text{———}(1)$$

given

$[A_0] = 0.02\text{M}$; $t_{1/2} = 10\,\text{min}$

$[A_0] = 0.04\text{M}$; $t_{1/2} = ?$

substitute in (1)

$10\text{ min} \propto 0.02\text{M}$ ———(2)

$t_{1/2} \propto 0.04\text{M}$ ———(3)

$$(3)\big/(2)$$

$$\Rightarrow \frac{t_{1/2}}{10\,\text{min}} = \frac{0.04\text{ M}}{0.02\text{ M}}$$

$$t_{1/2} = 2 \times 10\,\text{min} = 20\,\text{min}$$

3. option (b)

$$k = A\,e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

this equation is in the form of a straight line equatoion

$y = c + m\,x$

a plot of $\ln k$ vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

4. option(d)

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

$t_{1/2}$ does not depend on the initial concentration and it remains constant (whatever may be the initial concentration)

$t_{1/2} = 2.5$ hrs

5. option(c)

$$Rate = \left(\frac{-1}{2}\right)\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \left(\frac{1}{3}\right)\frac{d[H_2]}{dt}$$

$$\left(\frac{1}{2}\right)k_1[NH_3] = k_2[NH_3] = \left(\frac{1}{3}\right)k_3[NH_3]$$

$$\left(\frac{3}{2}\right)k_1 = 3k_2 = k_3$$

$$1.5\,k_1 = 3k_2 = k_3$$

6. option(c)

Given :

At low pressure the reaction follows first order, therefore

$Rate \; \alpha [\text{reactant}]^1$

$Rate \; \alpha \; (\text{surface area})$

At high pressure due to the complete coverage of surface area, the reaction follows zero order.

$Rate \; \alpha [\text{reactant}]^0$

Therefore the rate is independent of surface area.

7. option(b)

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

$$\text{rate} = \frac{-d[A]}{dt}$$

$$\text{unit of rate} = \frac{\text{mol L}^{-1}}{s} = \text{mol L}^{-1}s^{-1}$$

$$\text{unit of rate constant} = \frac{\left(\text{mol L}^{-1}s^{-1}\right)}{\left(\text{mol L}^{-1}\right)^n} = \text{mol}^{1-n}\ \text{L}^{n-1}s^{-1}$$

in this case

$$\text{rate} = k[\text{Acetone}]^{3/2}$$

$$n = 3/2$$

$$\text{mol}^{1-(3/2)}\ \text{L}^{(3/2)-1}s^{-1}$$

$$\text{mol}^{-(1/2)}\ \text{L}^{(1/2)}s^{-1}$$

8. option(b)

A catalyst provides a new path to the reaction with low activation energy. i.e., it lowers the activation energy.

9. option(a)

In zero order reactions, increase in the concentration of reactant does not alter the rate. So statement (i) is wrong.

$$k = A\,e^{-\left(\frac{E_a}{RT}\right)}$$

if $E_a = 0$ so, statement (ii) is correct, and statement (iii) is wrong

$$k = A\,e^0$$

$$k = A$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

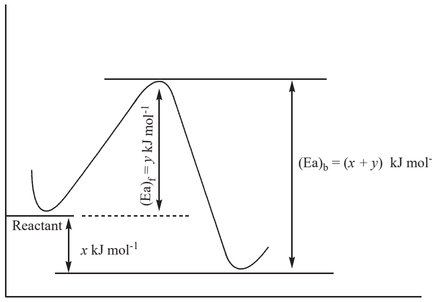
this equation is in the form of a straight line equatoion

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

a plot of lnk vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

so statements (iv) and (v) are wrong.

10. option(d)



$$(x + y)\,\text{kJmol}^{-1}$$
$$(x + y) \times 10^3\ \text{Jmol}^{-1}$$

11. option(c)

$$T_1 = 200\text{K} \ ;\ k = k_1$$
$$T_2 = 400\text{K} \ ;\ k = k_2 = 2k_1$$
$$\log\left(\frac{k_2}{k_1}\right) = \frac{2.303\ E_a}{R}\left(\frac{T_2 - T_1}{T_1\ T_2}\right)$$
$$\log\left(\frac{2\ k_1}{k_1}\right) = \frac{2.303\ E_a}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{400\ \text{K} - 200\text{K}}{200\text{K} \times 400\text{K}}\right)$$
$$E_a = \frac{0.3010 \times 8.314\ \text{J mol}^{-1} \times 200 \times 400}{2.303 \times 200}$$
$$E_a = 434.65\ \text{J mol}^{-1}$$

12. option(b)

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$
$$2.303 \times 10^{-2}\ \text{hour}^{-1} = \left(\frac{2.303}{1806\ \text{min}}\right)\log\left(\frac{0.25}{[A]}\right)$$
$$\left(\frac{2.303 \times 10^{-2}\ \text{hour}^{-1} \times 1806\ \text{min}}{2.303}\right) = \log\left(\frac{0.25}{[A]}\right)$$

$$\left(\frac{1806 \times 10^{-2}}{60}\right) = \log\left(\frac{0.25}{[A]}\right)$$

$$0.301 = \log\left(\frac{0.25}{[A]}\right)$$

$$\log 2 = \log\left(\frac{0.25}{[A]}\right)$$

$$2 = \left(\frac{0.25}{[A]}\right)$$

$$[A] = \left(\frac{0.25}{2}\right) = 0.125\text{M}$$

13. option(b)

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$[A_0] = 100\ ;\ [A] = 25$$

$$6.909 = \left(\frac{2.303}{t}\right)\log\left(\frac{100}{25}\right)$$

$$t = \left(\frac{2.303}{6.909}\right)\log(4)$$

$$t = \left(\frac{1}{3}\right)\log 2^2$$

$$t = \left(\frac{2}{3}\right)\log 2$$

14. option(c)

$$k = \left(\frac{1}{t}\right)\ln\left(\frac{[A_0]}{[A]}\right)$$

$$[A_0] = 0.1\ ;\ [A] = 0.05$$

$$k = \left(\frac{1}{t_{1/2}}\right)\ln\left(\frac{0.1}{0.05}\right)$$

$$k = \left(\frac{1}{t_{1/2}}\right)\ln(2)$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

15. option(b)

$$\text{rate}_1 = k[0.1]^n[0.1]^m \text{ ——(1)}$$

$$\text{rate}_2 = k[0.2]^n[0.1]^m \text{ ——(2)}$$

$$(2)/(1)$$

$$\frac{2x}{x} = \frac{k[0.2]^n[0.1]^m}{k[0.1]^n[0.1]^m}$$

$$\frac{2x}{x} = 2^n \quad \therefore\ n = 1$$

$$\text{rate}_3 = k[0.1]^n[0.2]^m \text{ ——(3)}$$

$$\text{rate}_4 = k[0.2]^n[0.2]^m \text{ ——(4)}$$

$$(4)/(2)$$

$$\frac{8x}{2x} = \frac{k[0.2]^n[0.2]^m}{k[0.2]^n[0.1]^m}$$

$$\frac{8}{2} = 2^m \quad \therefore\ m = 2$$

$$\therefore\ \text{rate} = k[A]^1[B]^2$$

16. option(c)

For a first reaction, If the concentration of reactant is doubled, then the rate of reaction also doubled.

Rate constant is independent of concentration and is a constant at a constant temperature,

17. option(a)

The unit of rate constant is s^{-1} and it indicates that the reaction is first order.

18. option(c)

$$Rate = \frac{d[N_2O_5]}{dt} = \left(\frac{1}{2}\right)\frac{d[NO_2]}{dt} = \frac{2\,d[O_2]}{dt}$$

Given that

$$\frac{d[N_2O_5]}{dt} = 6.5 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[NO_2]}{dt} = 2 \times 6.5 \times 10^{-2} = 1.3 \times 10^{-1} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[O_2]}{dt} = \frac{6.5\times10^{-2}}{2} = 3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$$

19. option(d)

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

$$Rate = \frac{-d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt}$$

$$\text{no of moles of oxygen} = \left(\frac{48}{32}\right) = 1.5 \text{ mol}$$

$\therefore$ rate of formation of oxygen = 2×1.5 = 3 mol min^{-1}

20. option(a)

For a first order reaction $t_{1/2}$ is independent of initial concentration .i.e., $\therefore$ $n \neq 1$; for such cases

$$t_{1/2}\ \alpha\ \frac{1}{[A_0]^{n-1}} \quad \text{------- (1)}$$

If $[A_0] = 2[A_0]$; then $t_{1/2} = 2t_{1/2}$

$$2\,t_{1/2}\ \alpha\ \frac{1}{[2\,A_0]^{n-1}} \quad \text{------ (2)}$$

$$\frac{(2)}{(1)} \Rightarrow$$

$$2 = \frac{1}{[2A_0]^{n-1}} \times \frac{[A_0]^{n-1}}{1}$$

$$2 = \frac{[A_0]^{n-1}}{[2A_0]^{n-1}}$$

$$2=\left(\frac{1}{2}\right)^{n-1}$$
$$2=\left(2^{-1}\right)^{n-1}$$
$$2^{1}=\left(2^{-n+1}\right)$$
$$n=0$$

21. Answer : option(a)

	A	$\longrightarrow$	B	C	D
Initial	a		0	0	0
Reacted at time t	x		x	x	x
After time t	$(a-x)$		x	x	x
Total number of moles		$=(a+2x)$			

$$a \propto P_0$$
$$(a+2x) \propto P$$
$$\frac{a}{(a+2x)}=\frac{P_0}{P}$$
$$x=\frac{(P-P_0)a}{2P_0}$$
$$(a-x)=a-\left(\frac{(P-P_0)a}{2P_0}\right)$$
$$(a-x)=a\left\{\frac{3P_0-P}{2P_0}\right\}$$
$$k=\left(\frac{2.303}{t}\right)\log\frac{[A_0]}{[A]}$$
$$k=\left(\frac{2.303}{t}\right)\log\left(\frac{a}{a-x}\right)$$
$$k=\left(\frac{2.303}{t}\right)\log\left(\frac{a}{a\left\{\frac{3P_0-P}{2P_0}\right\}}\right)$$
$$k=\left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0-P}\right)$$

22. Answer : option(d)5

$$t_{75\%} = 2t_{50\%}$$

$$t_{50\%} = \left(\frac{t_{75\%}}{2}\right) = \left(\frac{60}{2}\right) = 30\,\text{min}$$

23. Answer : option(d)

in140 days $\Rightarrow$ initial concentration reduced to $\left(\frac{1}{2}\right)g$

in 280 days $\Rightarrow$ initial concentration reduced to $\left(\frac{1}{4}\right)g$

in 420 days $\Rightarrow$ initial concentration reduced to $\left(\frac{1}{8}\right)g$

in 560 days $\Rightarrow$ initial concentration reduced to $\left(\frac{1}{16}\right)g$

24. Answer : option(b)

For a first order reaction

$$t_{1/2} = \frac{0.6932}{k}$$

For a second order reaction

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)\,k\,[A_0]^{n-1}}$$

$n = 2$

$$t_{1/2} = \frac{2^{2-1}-1}{(2-1)\,k\,[A_0]^{2-1}}$$

$$t_{1/2} = \frac{1}{k\,[A_0]}$$

25. Answer : option(c)

$$1 \xrightarrow{t_{1/2}} \left(\frac{1}{2}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{4}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{8}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{16}\right)$$

$\therefore\ 4\,t_{1/2} = 2$ hours

$t_{1/2} = 30$ min

Answer the following:

10 solution

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

(i) when $[L] = [4L]$

$$\text{Rate} = k[A]^2[B][4L]^{3/2}$$

$$\text{Rate} = 8\left(k[A]^2[B][L]^{3/2}\right)\text{-----(2)}$$

Comparing (1) and (2) ; rate is increased by 8 times.

(ii) when $[A] = [2A]\ and\ [B] = [2B]$

$$\text{Rate} = k[2A]^2[2B][L]^{3/2}$$

$$\text{Rate} = 8\left(k[A]^2[B][L]^{3/2}\right)\text{-----(3)}$$

Comparing (1) and (3) ; rate is increased by 8 times.

(iii) when $[A] = \left[\dfrac{A}{2}\right]$

$$\text{Rate} = k\left[\frac{A}{2}\right]^2[B][L]^{3/2}$$

$$\text{Rate} = \left(\frac{1}{4}\right)\left(k[A]^2[B][L]^{3/2}\right)\text{-----(4)}$$

Comparing (1) and (4) ; rate is reduced to ¼ times.

(iv) when $[A] = \left[\dfrac{A}{3}\right]\ and\ [L] = [4L]$

$$\text{Rate} = k\left[\frac{A}{3}\right]^2[B][4L]^{3/2}$$

$$\text{Rate} = \left(\frac{8}{9}\right)\left(k[A]^2[B][L]^{3/2}\right)\text{-----(5)}$$

Comparing (1) and (5) ; rate is reduced to 8/9 times.

11. solution

Let us consider the dimerisation of a monomer M

$$2M \longrightarrow (M)_2$$

$$\text{Rate} = k[M]^n$$

Given that n=2 and [M] = 0.05 mol L^{-1}

Rate = 7.5 X 10^{-3} mol $L^{-1}s^{-1}$

$$k = \frac{\text{Rate}}{[M]^n}$$

$$k = \frac{7.5\times10^{-3}}{(0.05)^2} = 3\ \text{mol}^{-1}\text{Ls}^{-1}$$

12. Solution

$$\text{rate} = k[x]^{\left(\frac{3}{2}\right)}[y]^{\left(\frac{1}{2}\right)}$$

$$\text{overall order} = \left(\frac{3}{2}+\frac{1}{2}\right) = 2$$

i.e., second order reaction.

Since the rate expression does not contain the concentration of z , the reaction is zero order with respect to z.

15. Solution:

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{1\,\text{min}}\log\frac{[0.08]}{[0.04]}$$

$$k = 2.303\log 2$$

$$k = 2.303\times0.3010$$

$$k = 0.6932\,\text{min}^{-1}$$

$$k = \left(\frac{0.6932}{60}\right)s^{-1}$$

$$k = 1.153\times10^{-2}\ s^{-1}$$

19. Solution

$$k = A\ e^{-\left(\frac{E_a}{RT}\right)}$$

$$k = 1.6\ \times10^{13}\text{s}^{-1}e^{-\left(\frac{200\times103\ \text{J mol}^{-1}}{8.314\,\text{JK}^{-1}\text{mol}^{-1}\times600\,\text{K}}\right)}$$

$$k = 1.6\ \times10^{13}\text{s}^{-1}\ e^{-(40.1)}$$

$$k = 1.6\ \times10^{13}\text{s}^{-1}\times3.8\times10^{-18}$$

$$k = 6.21\times10^{-5}\text{s}^{-1}$$

20. Solution

$$\text{rate} = k[x]^{n}[y]^{m}$$

$$0.15 = \mathrm{k}[0.2]^{n}[0.02]^{m} \text{———}(1)$$

$$0.30 = \mathrm{k}[0.4]^{n}[0.02]^{m} \text{———}(2)$$

$$1.20 = \mathrm{k}[0.4]^{n}[0.08]^{m} \text{———}(3)$$

$$(3)\big/(2)$$

$$\frac{1.2}{0.3} = \frac{\mathrm{k}[0.4]^{n}[0.08]^{m}}{\mathrm{k}[0.4]^{n}[0.02]^{m}}$$

$$4 = \left(\frac{[0.08]}{[0.02]}\right)^{m}$$

$$4 = (4)^{m}$$

$$\therefore\ m = 1$$

$$(2)\big/(1)$$

$$\frac{0.30}{0.15} = \frac{\mathrm{k}[0.4]^{n}[0.02]^{m}}{\mathrm{k}[0.2]^{n}[0.02]^{m}}$$

$$2 = \left(\frac{[0.4]}{[0.2]}\right)^{n}$$

$$2 = (2)^{n}$$

$$\therefore\ n = 1$$

$$\text{Rate } = \mathrm{k}\ [x]^{1}[y]^{1}$$

$$0.15\ = \mathrm{k}\ [0.2]^{1}[0.02]^{1}$$

$$\frac{0.15}{[0.2]^{1}[0.02]^{1}} = \mathrm{k}$$

$$\mathrm{k} = 37.5\ \mathrm{mol^{-1}L}\ s^{-1}$$

23**Solution:**

We know that, $t_{1/2} = 0.693/\mathrm{k}$

$t_{1/2} = 0.693/1.54\mathrm{x}\ 10^{-3}\ \mathrm{s}^{-1}$ = **450 s**

24.**Solution:**

We know that, $\mathrm{k} = 0.693/\ t_{1/2}$

$\mathrm{k} = 0.693/\ 8.0$ minutes = 0.087 minutes^{-1}

For a first order reaction,

$$\mathrm{t} = \frac{2.303}{\mathrm{k}}\log\frac{[\mathrm{A}_0]}{[\mathrm{A}]}$$

$$\mathrm{t} = \frac{2.303}{0.087\ \mathrm{min^{-1}}}\log\left(\frac{100}{1}\right)$$

$$\mathrm{t} = 52.93\,\mathrm{min}$$

25 **Solution:**

i) Order of a reaction = 1; $t_{1/2}$ = 60 ; seconds, k = ?

We know that, $\mathrm{k} = \dfrac{2.303}{t_{1/2}}$

$$\mathrm{k} = \frac{2.303}{60} = 0.01155\ s^{-1}$$

ii) $[\mathrm{A}_0] = 100\%$ t = 180 s , k = 0.01155 seconds^{-1}, $[\mathrm{A}]$ = ?

For the first order reaction

$$\mathrm{k} = \frac{2.303}{\mathrm{t}}\log\frac{[\mathrm{A}_0]}{[\mathrm{A}]}$$

$$0.01155 = \frac{2.303}{180}\log\left(\frac{100}{[\mathrm{A}]}\right)$$

$$\frac{0.01155\times180}{2.303} = \log\left(\frac{100}{[\mathrm{A}]}\right)$$

$$0.9207 = \log100 - \log[\mathrm{A}]$$

$$\log[\mathrm{A}] = \log100 - 0.9207$$

$$\log[\mathrm{A}] = 2 - 0.9207$$

$$\log[\mathrm{A}] = 1.0973$$

$$[\mathrm{A}] = \text{antilog of }(1.0973)$$

$$[\mathrm{A}] = 12.5\%$$

26 **Solution:**

i) Let A = 100M, $[\mathrm{A}_0]$–$[\mathrm{A}]$ = 20M,

For the zero order reaction

$$\mathrm{k} = \left(\frac{[\mathrm{A}_0]-[\mathrm{A}]}{\mathrm{t}}\right)$$

$$k=\left(\frac{20\text{M}}{20\text{min}}\right)=1\,\text{Mmin}^{-1}$$

Rate constant for a reaction = 1Mmin^{-1}

ii) To calculate the time for 80% of completion

$k = 1\text{Mmin}^{-1}$, $[A_0] = 100\text{M}$, $[A_0]-[A] = 80\text{M}$, $t = ?$

Therefore,

$$t=\left(\frac{[A_0]-[A]}{k}\right)=\left(\frac{80\text{M}}{1\text{Mmin}^{-1}}\right)=80\,\text{min}$$

27 Solution:

Here, we are given that

$E_a = 22.5 \text{ kcal mol}^{-1} = 22500 \text{ cal mol}^{-1}$

$T = 40°\text{C} = 40 + 273 = 313 \text{ K}$

$k = 1.8 \times 10^{-5} \text{ sec}^{-1}$

Substituting the values in the equation

$$\log A=\log k+\left(\frac{E_a}{2.303RT}\right)$$

$$\log A=\log\left(1.8\times10^{-5}\right)+\left(\frac{22500}{2.303\times1.987\times313}\right)$$

$$\log A=\log\left(1.8\right)-5+\left(15.7089\right)$$

$$\log A=10.9642$$

$$A=\text{antilog}\left(10.9642\right)$$

$$A=\ 9.208\times10^{10}\text{collisions s}^{-1}$$

28.**Solution:**

For a first order reaction

$$k=\frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k=\frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

In the present case, $V_\infty = 58.3$ ml.

The value of *k* at different time can be calculated as follows:

t (*min*)	V_t	V_∞ - V_t	$\frac{2.303}{t}\log\frac{V_\circ}{V_\circ - V_t}$
6	19.3	58.3-19.3 = 39.0	$k=\frac{2.303}{6}\log\left(\frac{58.3}{39}\right)$ = 0.0670 min^{-1}
12	32.6	58.3-32.6 = 25.7	$k=\frac{2.303}{12}\log\left(\frac{58.3}{25.7}\right)$ = 0.0683 min^{-1}
18	41.3	58.3-41.3 = 17.0	$k=\frac{2.303}{18}\log\left(\frac{58.3}{17}\right)$ = 0.0685 min^{-1}
24	46.5	58.3-46.5 = 11.8	$k=\frac{2.303}{24}\log\left(\frac{58.3}{11.8}\right)$ = 0.0666 min^{-1}

Since the value of k comes out to be nearly constant, the given reaction is of the first order. The mean value of $k = 0.0676\ \text{min}^{-1}$

29.**Solution:**

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{V_0}{V_t}\right)$$

In the present case, $V_o = 46.1$ ml.

The value of k at each instant can be calculated as follows:

t (*min*)	V_t	$k = \left(\frac{2.303}{t}\right)\log\left(\frac{V_0}{V_t}\right)$
10	29.8	$k = \frac{2.303}{10}\log\left(\frac{46.1}{29.8}\right) = 0.0436\ \text{min}^{-1}$
20	19.3	$k = \frac{2.303}{20}\log\left(\frac{46.1}{19.3}\right) = 0.0435\ \text{min}^{-1}$

Thus, the value of k comes out to be nearly constant. Hence it is a reaction of the first order.

30. Solution:

i) For the first order reaction $k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$

Assume, $[A_0] = 100\ \%$, $t = 50$ minutes

Therefore, $[A] = 100 - 40 = 60$

$k = (2.303 / 50) \log (100 / 60)$

$k = 0.010216\ \text{min}^{-1}$

Hence the value of the rate constant is $0.010216\ \text{min}^{-1}$

ii) t = ?, when the reaction is 80% completed,

$[A] = 100 - 80 = 20\,\%$

From above, $k = 0.010216\ \text{min}^{-1}$

$t = (2.303 / 0.010216) \log (100 / 20)$

$t = 157.58$ min

The time at which the reaction will be 80% complete is 157.58 min.