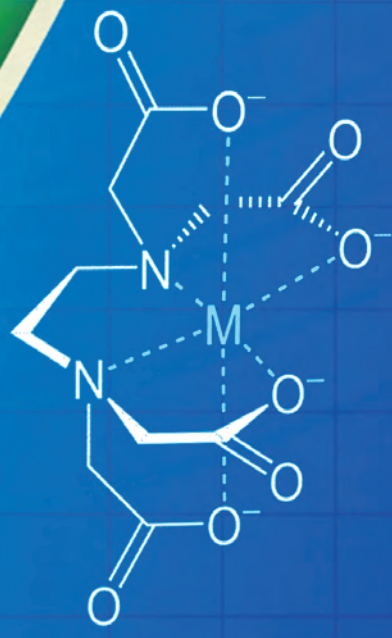
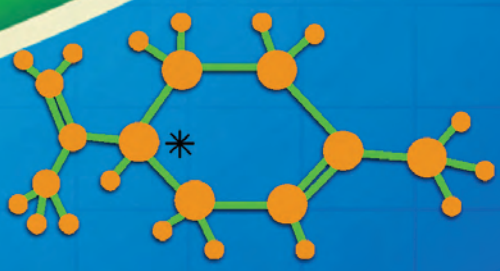
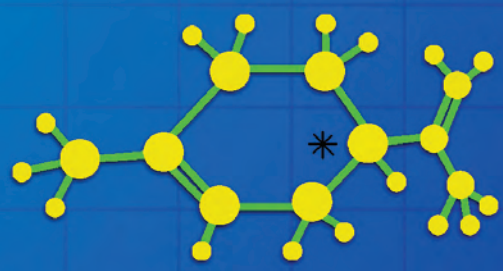
CHEMISTRY

Standard XII







The Constitution of India

Chapter IV A

Fundamental Duties

ARTICLE 51A

Fundamental Duties- It shall be the duty of every citizen of India–

(a) to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;

(b) to cherish and follow the noble ideals which inspired our national struggle for freedom;

(c) to uphold and protect the sovereignty, unity and integrity of India;

(d) to defend the country and render national service when called upon to do so;

(e) to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities, to renounce practices derogatory to the dignity of women;

(f) to value and preserve the rich heritage of our composite culture;

(g) to protect and improve the natural environment including forests, lakes, rivers and wild life and to have compassion for living creatures;

(h) to develop the scientific temper, humanism and the spirit of inquiry and reform;

(i) to safeguard public property and to abjure violence;

(j) to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement;

(k) who is a parent or guardian to provide opportunities for education to his child or, as the case may be, ward between the age of six and fourteen years.

The Coordination Committee formed by GR No. Abhyas - 2116/(Pra.Kra.43/16) SD - 4 Dated 25.4.2016 has given approval to prescribe this textbook in its meeting held on 30.01.2020 and it has been decided to implement it from academic year 2020-21.

CHEMISTRY

STANDARD TWELVE

R5W2F5

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2020

Maharashtra State Bureau of Textbook Production and Curriculum Research, Pune.

First Edition : 2020
Reprint : 2022

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Paper
70 GSM Creamwove
Print Order
N/PB/2022-23/60,000
Printer
RUNA GRAPHICS, PUNE

Production
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The Constitution of India

Preamble

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC and to secure to all its citizens:

JUSTICE, social, economic and political;

LIBERTY of thought, expression, belief, faith and worship;

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the unity and integrity of the Nation;

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949, do HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.

NATIONAL ANTHEM

Jana-gana-mana-adhināyaka jaya hē
Bhārata-bhāgya-vidhātā,

Panjāba-Sindhu-Gujarāta-Marāthā
Drāvida-Utkala-Banga

Vindhya-Himāchala-Yamunā-Gangā
uchchala-jaladhi-taranga

Tava subha nāmē jāgē, tava subha āsisa māgē,
gāhē tava jaya-gāthā,

Jana-gana-mangala-dāyaka jaya hē
Bhārata-bhāgya-vidhātā,

Jaya hē, Jaya hē, Jaya hē,
Jaya jaya jaya, jaya hē.

PLEDGE

India is my country. All Indians are my brothers and sisters.

I love my country, and I am proud of its rich and varied heritage. I shall always strive to be worthy of it.

I shall give my parents, teachers and all elders respect, and treat everyone with courtesy.

To my country and my people, I pledge my devotion. In their well-being and prosperity alone lies my happiness.

Preface

Dear Students,

We welcome you all to std. XII. For the first time, you were introduced to the subject of chemistry discipline in std XI.

Chemistry is very vast subject that covers many aspects of our everyday experience. This textbook aims to create awareness and to understand certain essential aspects by the national curriculum framework (NCF) which was formulated in 2005, followed by the state curriculum framework (SCF) in 2010. Based on these two frameworks, reconstruction of the curriculum and prepartion of a revised syllabus has been done and designed now.

Three major branches of chemistry, namely organic chemistry, inorganic chemistry and physical chemistry are presented in separate units in this book. Care is taken to have an integrated approach in deliberation of their contents. Chemistry is highly applied subject. In the unit "applied chemistry" along with the application of chemistry in life science and materials in everyday life, the upcoming applied branches, namely nanochemistry and green chemistry are also introduced. You can learn basic principles, understand facts and put them into practice by learning in the classroom and laboratory. The textbook is presented in a simple language with relevant diagrams, graphs, tables, photographs. This will help you to understand various terminology, concepts with more clarity. All the illustrations are in colour form. The new syllabus focuses on the basic principles, concepts, laws based on precise observations, their applications in everyday life and ability to solve different types of problems. The general teaching - learing objectives of the revised syllabus are further determined on the basis of the 'Principle of constructivism' i.e. self learning.

The curriculum and syllabus is designed to make the students to think independently. The students are encouraged to read, study more through the additional information given in the colored boxes. Activities have been introduced in each chapter. These activities will help to understand the content knowledge on your own efforts. QR code has been introduced for gaining the additional information, abstracts of chapters and practice questions/ activities.

The efforts taken to prepare the text book will help the students think about more than just the content of the chemical concepts. Teachers, parents as well as the aspiring condidates preparing for the competitive examinations will be benefited.

We look forward to a positive response from the teachers and students.

Our best wishes to all !

(Vivek Gosavi)
Director
Maharashtra State Bureau of Textbook
Production and Curriculum Research, Pune 4

Pune
Date : 21 February 2020
Bharatiya Saur : 2 Phalguna 1941

- For Teachers -

Dear Teachers,

We are happy to introduce the revised textbook of chemistry for std. XII. This book is a sincere attempt in continuation with the standard XI book to follow the maxims of teaching as well as develop a 'constructivist' approach to enhance the quality of learning. The demand for more activity based, experiential and innovative learning opportunities is the need of the time. The present curriculum has been restructured so as to bridge the credibility gap that exists in the experience in the outside world. Guidelines provided below will help to enrich the teaching - learning process and achieve the desired learning outcomes.

- To begin with, get familiar with the textbook yourself.
- The present book has been prepared for constructivism and activity based learning.
- Teachers must skilfully plan and organize the activities provided in each chapter to develop interest as well as to stimulate the thought process among the students.
- Always teach with proper planning.
- Use teaching aids as required for the proper understanding of the subject.
- Do not finish the chapter in short.
- Follow the order of the chapters strictly as listed in the contents because the units are introduced in a graded manner to facilitate knowledge building.
- Each unit is structured in a definite manner. It starts from the basic concepts of general chemistry required for each branch of chemistry. Application of this knowledge will help students to understand further chapters in each unit.
- Each chapter provides solved problems on each and every concept and various laws. The solved problems are put into boxes. Teachers should explain each step of the problems to the student and give them practice.
- Invite students' participation by making use of the boxes like 'Can You Recall', 'Do you know?'
- Encourage the students to collect related information by providing them the websites.
- Teaching- learning interactions, processes and participation of all students are necessary and so is your active guidance.
- Do not use the content of the boxes titled 'Do you know'? for evaluation.
- Exercises include parameters such as co-relation, critical thinking, analytical reasoning etc. Evaluation pattern should be based on the given parameters. Use different combinations of questions.
- Illustrative figures are included to help assimilation of new concepts. Teachers should note that students are not expected to draw all the figures included in this book. As a part of evaluation students can be asked to draw schematic diagrams/structures and interpret or label other complicated figures.

Can you recall ? 

Remember... 

Do you know ? 

Observe and discuss... 

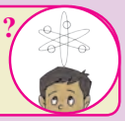
Use your brain power 

Can you tell ? 

Internet my friend 

Try this... 

Activity : 

Can you think ? 

Cover page :

- **(+) - Limonene and (-) Limonene :** major contributors to the characteristic flavours of peelings of oranges and lemons respectively.
- **Image of gold surface :** Au (111), obtained by Scanning Tunneling Microscope (STM).
- **Structures of coordination complexes :** haemoglobin, chlorophyll and metal -EDTA complex.

Competency Statements - Standard XII

Area/ Unit/ Lesson	After studying the contents in Textbook students.....
Physical Chemistry	• Distinguish crystal structures illustrating unit cell and packing efficiency in cubic systems. • Gain information on point defects and band theory in relation to electric and magnetic behavior. • Define solubility and rationalise its dependence on various factors. • Explain Henry and Raoult's laws. • Derive expressions for colligative properties. • Learn van't Hoff factor and its correlation with dissociation constant. • Catagorize strong and weak acid bases. • Learn Ostwald's dilution law. • Derive Henderson Balch Hassel equation. • Explain the role of buffer solutions in controlling of pH. • Understand spontaneity of reactions. • Know reversible/irreversible processes and PV work. • Understand first and second laws of thermodynamics. • Work out change in enthalpy, entropy and Gibbs' functions in physical and chemical transformations. • Apply Hess's Law in thermochemical equations. • State what are strong and weak electrolytes. • Define Kohlrausch law and state its importance. • Understand functioning of electrolytic and galvanic cells. Write half cell reactions there in. • Describe type of electrodes. • Derive Nernst equation and understand its importance. • Know what are dry cell, lead strong batteries and fuel cells. • Describe the electrochemical series and its implications. • Define average and instantaneous rate, order and molecularity in kinetics • Formulate differential and integral rate laws for zero and first order reactions. • Understand basis of collision theory of reaction rates • Sketch qualitatively potential energy curve. Understand acceleration of reactions in the presence of catalyst. • Solve relevant numerical problems.
Inorganic chemistry	• Write electronic configuration of groups 16, 17, 18 and those of d and f blocks. • Correlate atomic properties of elements with electron configuration. • Explain the anomalous behaviour of 'O' and 'F'. • Understand allotropy in 'O' and 'S'. • Draw structures of oxyacids of 'sulfur' and 'halogens'. • Write reactions for preparation, chemical properties of O_2, O_3, SO_2, H_2SO_4, Cl_2, HCl, $KMnO_4$, $K_2Cr_2O_7$. • Draw structures of interhalogen and xenon compounds and illustrate their properties. State the methods of preparation with reaction. • Know chemistry of the elements belonging to groups 16, 17, 18. • Understand the principles of metallurgy in extraction of iron. • Compare lanthanoides and actinoides. • Enlist properties of the manmade post actinoide elements. • Understand Werner theory of coordination compounds. • Understand and apply EAN rule for stability of coordination compounds. • Understand diverse isomerism in coordination compounds. • Use the concept of hybridization for predicting structures and magnetic behaviour of complexes based on the V.B.T. • Understand C.F.T. Sketch qualitatively d-orbital splitting diagrams in octahedral and tetrahedral ligand field environments. • Distinguish between high spin and low spin complexes. • Predict structure, colour and magnetic properties of the complexes based on the C.F.T.

Organic Chemistry	• State common and IUPAC names of compounds and methods of preparation of halogen derivatives, alcohols, phenols, ethers, aldehydes, ketones, carboxylic acid and amines. • Understand structure, chemical properties, laboratory tests and reactions of the above functional groups. • Explain acid or base strength of alcohols, phenols, carboxylic acids and amines. • Explain trends in boiling point and solubility of compounds of above functional groups in terms of intermolecular forces. • Understand optical activity, recognize chiral molecules and represent with Fischer projection and wedge formulae. • Understand mechanism of nucleophilic substitution reactions and influencing factors.
Applied Chemistry	• Classify carbohydrates, amino acids, nucleic acids. • Represent monosaccharides using the Fischer projection formula. • Represent monosaccharides, disaccharides and polysaccharides using the Haworth formula. • Correlate properties of carbohydrates to the presence or absence of potential aldehyde group. • Learn four level structure of proteins and primary structures nucleic acid. • Represent primary structure of dipeptide and tripeptide from data on the terminals. • Understand enzyme catalysis and double strand DNA structure. • Understand classification of polymers on the basis of source, structure, intermolecular forces, polymerization, number of monomers and biodegradability. • Understand addition and condensation polymerization. • Know properties, structure and preparation of natural rubber, vulcanized rubber, Buna-S, viscose, LDP, HDP, teflon, polyacrylo nitrile, polyamide, polyesters, phenol-formaldehyde resin and PHBV. • Understand scope of green chemistry with reference to sustainable development. • Recognize twelve principles of green chemistry and their implementation. • Correlate the Chemistry knowledge gained so far as pro or counter to the principles of green chemistry. • Understand scope and applications of nanochemistry. • Gain knowledge of a synthetic method and properties of nanoparticles. • Know instrumental techniques for characterization of nanomaterials.

CONTENTS

1. SOLID STATE

Can you recall ?

- What are the three most common states of matter?
- How does solid state differ from the other two states ? (Answer with reference to volume, shape, effect of temperature and pressure on these and the motion of constituent particles and interparticle forces.)

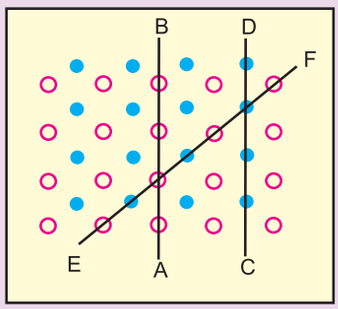
1.1 Introduction : As studied earlier, the solid state of matter is characterised by strong interparticle forces of attraction. As a result most solids have definite shape and volume, which change only slightly with change in temperature and pressure. The smallest constituent particles of various solids are **atoms**, **ions** or **molecules**. All such smallest constituent particles of solids will be referred to as '**particles**' in this chapter.

1.2 Types of solids : There are two types of solids, namely crystalline solids and amorphous solids.

Observe and discuss...

- Collect the following solids : grannular sugar, common salt, blue vitriol.
- Observe a few grannules of these solids under a magnifying lens or microscope.
- Discuss your observations with reference to the following points : (i) Shape of the grannules, (ii) Smoothness of faces of the grannules and (iii) Angles between various edges of the grannules.
- All the above solids are crystalline solids. Name the properties of crystals that you observed in this activity.


Try this...



● Particle 1 ○ Particle 2

Observe the above figure carefully. The two types of circles in this figure represent two types of constituent particles of a solid.

- Will you call the arrangement of particles in this solid regular or irregular ?
- Is the arrangement of constituent particles same or different in directions $\overrightarrow{AB}$, $\overrightarrow{CD}$, and $\overrightarrow{EF}$?

1.2.1 Crystalline solids : Study of many crystalline solids indicates that they possess the following characteristic properties.

i. There is a **regularity** and **periodicity** in the arrangement of constituent particles in crystalline solids. The ordered arrangement of particles extends over a long range.

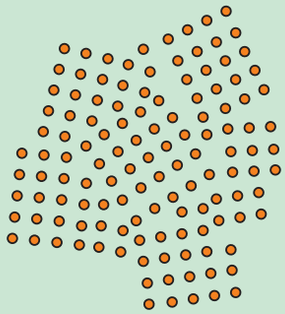
ii. Crystalline solids have **sharp melting points**, that is, they melt at a definite temperature.

iii. All crystalline substances except those having cubic structure are **anisotropic**. In other words their properties like refractive index, thermal and electrical conductivity, etc, are different in different directions.

Ice, salts such as NaCl, metals such as sodium, gold, copper and materials such as diamond, graphite, ceramics are examples of crystalline solids.

Do you know ?

- A single crystal has ordered (regular and periodic) arrangement of constituent particles throughout its bulk.
- Majority of crystalline solids, including metals, are polycrystalline in nature. Single grannule of a polycrystalline solid is made of many single crystals or crystallites packed together with different orientations.
- Single crystals are difficult to obtain. Diamond is an example of naturally formed single crystal.



1.2.2 Amorphous solids : The particles of a liquid are in constant motion. The stop action photograph of a liquid describes the amorphous state. In fact, they are supercooled liquids. Amorphous solids have the following characteristics.

i. The constituent particles in amorphous solids are **randomly arranged**. The particles do not have long range ordered structure, but they do have a short range order.

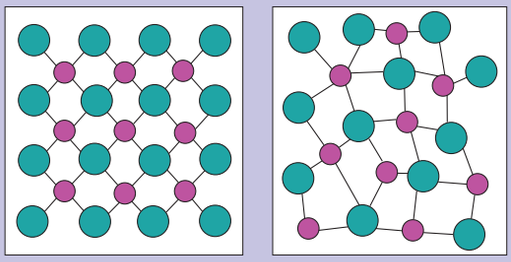
ii. Amorphous solids do not have sharp melting points. They melt gradually over a **temperature interval**. On heating, amorphous solids gradually and continuously soften and start to flow.

iii. These solids are **isotropic**. In other words, their properties such as refractive index, conductivity are all independent of direction of measurement. They exhibit the same magnitude for any property in every direction.

Glass, plastic, rubber, tar, and metallic glass (metal-metalloid alloy) are a few examples of amorphous solids.

Use your brain power

Identify the arrangements A and B as crystalline or amorphous.



1.2.3 Isomorphism and polymorphism

Similarity or dissimilarity in crystal structure of different solids is described as isomorphism and polymorphism.

i. Isomorphism : Two or more substances having the same crystal structure are said to be isomorphous. In these substances the chemical composition has the same atomic ratio. For example (i) NaF and MgO (ii) $NaNO_3$ and $CaCO_3$ are isomorphous pairs, and have the same atomic ratios, 1:1 and 1:1:3, respectively, of the constituent atoms.

ii. Polymorphism : A single substance that exists in two or more forms or crystalline structures is said to be polymorphous. Polymorphs of a substance are formed under different conditions. For example : Calcite and aragonite are two forms of calcium carbonate; α-quartz, β-quartz and cristobalite are three of the several forms of silica. Polymorphism occuring in elements is called **allotropy**. For example: three polymorphic (allotropic) forms of carbon are diamond, graphite and fullerene.

Do you know ?

Many crystalline forms of silica (SiO_2) are found in nature. Three of them are α-quartz, β-quartz and cristobalite

cristobalite

α-quartz

β-quartz

1.3 Classification of crystalline solids : Crystalline solids are further classified into four categories : ionic solids, covalent network solids, molecular solids and metallic solids.

1.3.1 Ionic crystals : Ionic crystals have the following characteristics :

i. The constituent particles of ionic crystals are **charged ions**. The cations and anions may differ in size.

ii. Each ion of a given sign of charge is bonded to ions of opposite charge around it by coulomb force. In other words, the particles of ionic crystals are held by **electrostatic force of attraction** between oppositely charged ions.

iii. Ionic crystals are **hard** and **brittle**. They have **high melting points**.

iv. These are **nonconductors of electricity** in solid state. However, they are good conductors when melted or dissolved in water.

For example : NaCl, K_2SO_4, CaF_2, KCl are ionic crystals.

1.3.2 Covalent network crystals

Characteristics of covalent network crystals are as follows :

i. The constituent particles in covalent network solids are **atoms**.

ii. The atoms in these crystals are linked by a continous system of **covalent bonds**. The result is a rigid three dimensional network that forms a giant molecule. The entire crystal is a single molecule.

iii. As a result of rigid and strongly bonded structure, covalent network crystals are **very hard**. In fact they are the hardest and most **incompressible** of all the materials. These crystals have **high melting and boiling points**.

iv. The electrons are localised in covalent bonds and hence are not mobile. As a result, covalent solids are **poor conductors** of heat and electricity.

For example : diamond, quartz (SiO_2), boron nitride, carborandum are covalent network solids.

Do you know ?

Diamond is the hardest known material.

Try this...

Graphite is a covalent solid yet soft and good conductor of electricity. Explain.

Can you recall ?

- What are structures of diamond and graphite ?
- What are the types of covalent bonds those link carbon atoms in diamond and graphite ?
- Are all the valence electrons of carbon atoms in graphite localized to specific covalent bonds ?

Remember...

Both ionic and covalent crystals are hard and have high melting and boiling points. We can use electrical properties to distinguish between them. Both are insulators at low temperature.

Ionic solids become good conductors only at high temperature, above their melting points.

The conductivity of covalent solids is in general low and increases with temperature. However, there is no abrupt rise in conductivity when substance is melted.

1.3.3 Molecular crystals : Substances such as Cl_2, CH_4, H_2, CO_2, O_2 on solidfication give molecular crystals. Crystalline organic compounds are also molecular solids.

i. The constituent particles of molecular solids are **molecules** (or unbonded single atoms) of the same substance.

Can you recall ?

What is a hydrogen bond ?

ii. The bonds within the molecules are covalent. The molecules are held together by various intermolecular forces of **attraction**. (Refer to XI Std. Chemistry Textbook, Chapter 10). For example :

   a. **Weak dipole-dipole interactions** in polar molecules such as solid HCl, H_2O, SO_2, which possess permanent dipole moment.

   b. **Very weak dispersion or London forces** in nonpolar molecules such as solid CH_4, H_2. These forces are also involved in monoatomic solids like argon, neon. (These substances are usually gases at room temperature.)

   c. **Intermolecular hydrogen bonds** in solids such as H_2O (ice), NH_3, HF and so forth.

iii. Because of weak intermolecular attractive forces, molecular solids are usually soft substances with **low melting points**.

iv. These solids are **poor electrical conductors** and are good insulators.

1.3.4 Metallic crystals : These are crystalline solids formed by atoms of the same metallic element, held together by a metallic bond.

Metallic bond : In a solid metal, the valence electrons are delocalised over the entire crystal leaving behind positively charged metal ions. Therefore, metallic crystals are often described as an array of positive ions immersed in a sea of mobile electrons. The attractive interactions between cations and mobile electrons constitute the metallic bonds. (For more details refer to section 1.9.2)

Metallic crystals have the following properties:

i. Metals are **malleable**, that is, they can be hammered into thin sheets.

ii. Metals are **ductile**, that is, they can be drawn into wires.

iii. Metals have **good electrical and thermal conductivity**.

Examples : metals such as Na, K, Ca, Li, Fe, Au, Ag, Co, etc.

The properties of different types of crystalline solids are summarized in Table 1.1.

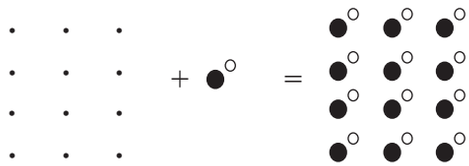
1.4 Crystal structure : The ordered three dimensional arrangement of particles in a crystal is described using two terms, namely, lattice and basis.

1.4.1 Crystal, lattice and basis : Lattice is a geometrical arrangement of points in a three dimensional periodic array. A crystal structure is obtained by attaching a constituent particle to each of the lattice points. Such constituent particles that are attached to the lattice points form the basis of the crystal lattice. Crystal

Table 1.1 : Properties of four types of crystalline solids

Property \ Type	Ionic solids	Covalent network solids	Molecular solids	Metallic solids
1. Particles of unit cell	Cations and anions	Covalently bonded atoms	Monoatomic or polyatomic molecules	Metallic ions in a sea of electrons
2. Interparticle forces	Electrostatic	Covalent bonds	London, dipole-dipole forces and/ or hydrogen bonds	Metallic bonds (attraction between cations and mobile valence electrons)
3. Hardness	Hard and brittle	Very hard	Soft	Variable from soft to very hard
4. Melting points	High 600^0C to 3000^0C	High 1200^0C to 4000^0C	Low (-272^0C to 400^0C)	Wide range (-39^0C to 3400^0C)
5. Thermal and electrical conductivity	Poor electrical conductors in solid state. Good conductors when melted or dissolved in water	Poor conductors Exceptions : i. Graphite : good conductor of electricity. ii. Diamond : good conductor of heat	poor conductor of heat and electricity	good conductor of heat and electricity
6. Examples	NaCl, CaF_2	diamond, silica	ice, benzoic acid	Na, Mg, Cu, Au

lattice is also called space lattice of crystal. Thus, crystal is the structure that results by attaching a basis to each of the lattice points. It is represented by the following equation.



Lattice + Basis = Crystal

1.4.2 Unit Cell : The space lattice of a crystal is built up of a three dimensional basic pattern. This basic pattern is repeated in three dimensions to generate the entire crystal. **The smallest repeating structural unit of a crystalline solid is called unit cell**.

When the unit cells are stacked together to generate the crystal, each unit cell shares its faces, edges and corners with neighbouring unit cells. It is important to understand that the geometric shape of a unit cell is same as that of the macroscopic crystal. For example, if the crystal has cubic shape the unit cell will also have its constituent particles arranged to form a tiny cube.

The dimensions of unit cell along the three axes are denoted by the symbols a, b and c. The angles between these axes are represented by the symbols $\propto$, β and γ as shown in Fig 1.1.

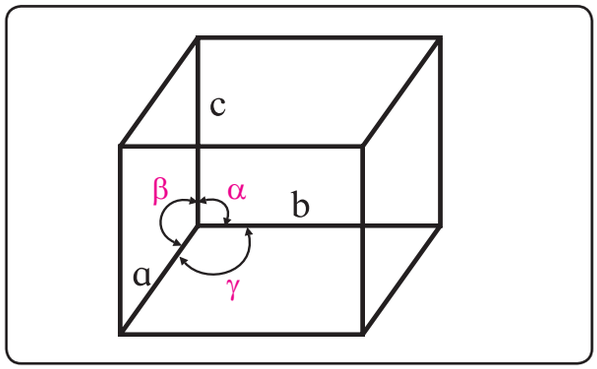


Fig. 1.1 : Unit cell parameters

1.4.3 Types of unit cell : There are four types of unit cells.

i. Primitive or simple unit cell : In primitive unit cell, the constituent particles are present at its corners only.

ii. Body-centred unit cell : In this type of unit cell, one constituent particle is present at the centre of its body in addition to the corner particles.

iii. Face-centred unit cell : This unit cell consists of particles at the centre of each of the faces in addition to the corner particles.

iv. Base-centred unit cell : This unit cell consists of particles at the centre of any two of its opposite faces in addition to the corner particles.

1.4.4 Crystal systems : By mathematical analysis, it has been proved that only fourteen different kinds of space lattices are possible. In other words, there are only 14 ways in which similar points can be arranged in a three dimensional order. These 14 lattices, which describe the crystal structure, are called **Bravais lattices**.

Fourteen Bravais lattices are divided into seven crystal systems. The possible combinations of lattice point spacings (a, b and c) along three axes and the angles ($\propto$, β and γ) between these axes give rise to seven crystal systems. In other words, seven crystal systems are associated with 14 Bravais lattices also called 14 unit cells.

The seven crystal systems are named as cubic, tetragonal, orthorhombic, rhombohedral, monoclinic, triclinic and hexagonal system. Cubic system will be discussed in the following section.

1.5 Cubic system : There are three kinds of unit cells in cubic system : primitive or simple cubic (sc), body-centred cubic (bcc) and face-centred cubic (fcc) (Fig. 1.2).

i. Simple cubic unit cell (sc) has a particle at each of the eight corners of a cube.

ii. Body-centred cubic unit cell (bcc) has particles at its eight corners and an additional particle in the center of the cube.

iii. Face-centred cubic unit cell (fcc) has particle at the centre of each of six faces in addition to the particles at eight corners of the cube.

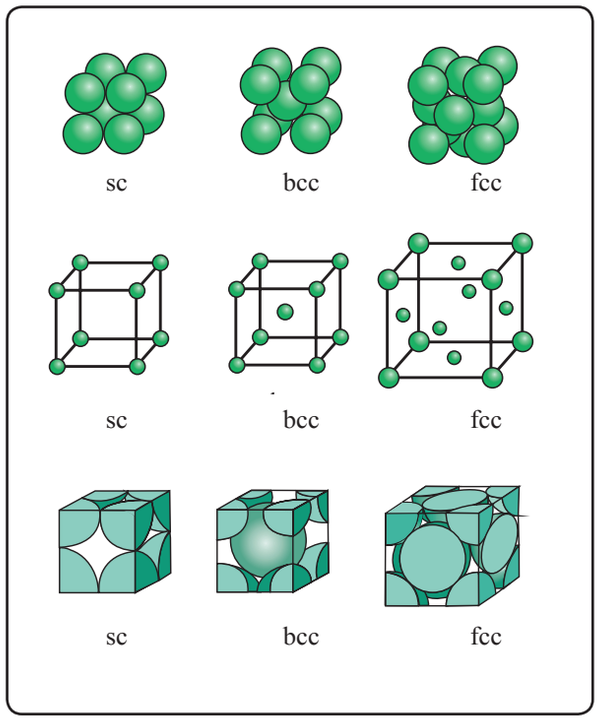


Fig. 1.2 : Cubic unit cell

1.5.1 Number of particles in cubic unit cells

i. Primitive or simple cubic unit cell (sc) : A simple cubic cell has particles at its eight corners. When these unit cells are stacked together, particle at each corner of a given unit cell is shared with seven other neighbouring cubes that come together at that corner. As a result the corner particle contributes its $1/8^{th}$ part to the given unit cell. Thus, a **simple cubic cell has** $1/8 \times 8 =$ **1 particle per unit cell**.

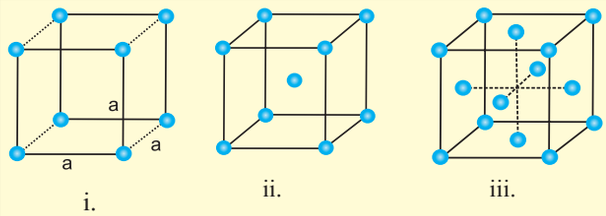
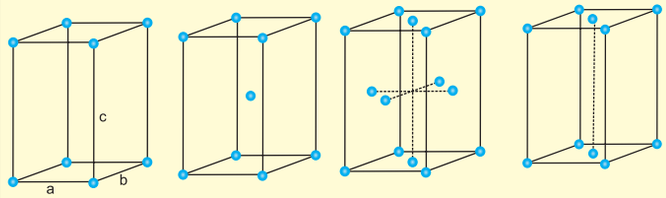
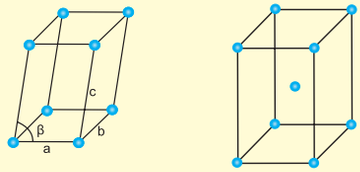
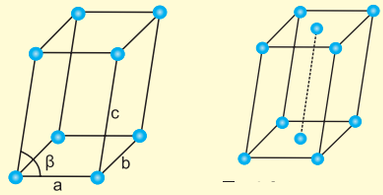
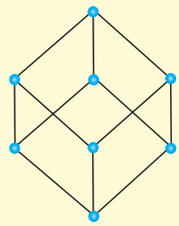
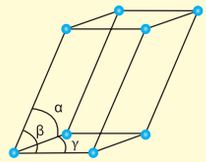
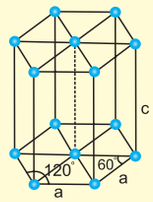
ii. Body-centred cubic unit cell (bcc) : A bcc unit cell has eight corner particles and an additional particle at the centre of the cube. One eighth of each particle from eight corners belongs to the given unit cell as mentioned in simple cubic unit cell.

The particle at the centre of a given cube is not shared by any other cube. Hence, it belongs entirely to the given unit cell. Thus bcc unit cell has one particle from eight corners plus one particle in the centre of the cube, making total of **2 particles per bcc unit cell**.

iii. Face-centred cubic unit cell (fcc) : A fcc unit cell has particles at the eight corners plus particles at the centre of its six faces. As described in simple cubic unit cell, one particle

Do you know ?

The names of fourteen Bravais lattices (unit cells) for each of the seven crystal system are shown below.

Crystal system	Bravais lattices	
	Name	unit cell structure
1. Cubic	i. simple or primitive ii. body-centred iii. face-centred	 i. ii. iii.
2. Orthorhombic	i. simple or primitive ii. body-centred iii. face-centred iv. base-centred	 i. ii. iii. iv.
3. Tetragonal	i. simple or primitive ii. body-centred	 i. ii.
4. Monoclinic	i. simple or primitive ii. base centred	 i. ii.
5. Rhombohedral	i. simple or primitive	
6. Triclinic	i. simple or primitive	
7. Hexagonal	i. simple or primitive	

from eight corners belongs to the given unit cell.

Each particle at the centre of the six faces is shared with one neighbouring cube. Thus,1/2 of each face particle belongs to the given unit cell. From six faces, 1/2 × 6 = 3 particles belong to the given unit cell.

Therefore, **fcc unit cell has** one corner particle plus 3 face particles, **total 4 particles per unit cell**.

Remember...

Each corner particle of a cube is shared by 8 cubes, each face particle is shared by 2 cubes and each edge particle is shared by 4 cubes.

1.5.2 Relationship between molar mass, density of the substance and unit cell edge length, is deduced in the following steps

i. If edge length of cubic unit cell is ***a***, the volume of unit cell is a^3.

ii. Suppose that mass of one particle is ***m*** and that there are ***n*** particles per unit cell.

$$\text{Mass of unit cell} = m \times n \quad \text{.....(1.1)}$$

iii. The density of unit cell (ρ), which is same as density of the substance is given by

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{m \times n}{a^3} = \text{density of substance} \quad \text{.....(1.2)}$$

iv. Molar mass (M) of the substance is given by

M = mass of one particle × number of particles per mole

$= m \times N_A$ (N_A is Avogadro number)

Therefore, $m = M/N_A$ .....(1.3)

v. Combining Eq. (1.1) and (1.3), gives

$$\rho = \frac{n\,M}{a^3\,N_A} \quad \text{.....(1.4)}$$

By knowing any four parameters of Eq. (1.4), the fifth can be calculated

Problem 1.1 : When gold crystallizes, it forms face-centred cubic cells. The unit cell edge length is 408 pm. Calculate the density of gold. Molar mass of gold is 197 g/mol.

Solution :

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

M = 197 g mol^{-1}, n = 4 atoms for fcc, $N_A = 6.022 \times 10^{23}$ atoms mol^{-1},

a = 408 pm = 408×10^{-12}m = 4.08×10^{-8} cm

Substitution of these quantities in the equation gives

$$\rho = \frac{197\ \text{g}\ \cancel{\text{mol}^{-1}} \times 4\ \cancel{\text{atom}}}{(4.08\times10^{-8})^3\ \text{cm}^3 \times 6.022\times10^{23}\ \cancel{\text{atom}}\ \cancel{\text{mol}^{-1}}}$$

$= 19.27\ \text{g/cm}^3$, $19.27 \times 10^3\ \text{kg/m}^3$.

1.6 Packing of particles in crystal lattice

Constituent particles of a crystalline solid are close packed. While describing the packing of particles in a crystal, the individual particles are treated as hard spheres. The closeness of particles maximize the interparticle attractions.

The number of **neighbouring spheres that touch any given sphere is its coordination number**. Magnitude of the coordination number is a measure of compactness of spheres in close-packed structures. The larger the coordination number, the closer are the spheres to each other.

1.6.1 Close packed structures : The three dimensional close packed structure can be understood conveniently by looking at the close packing in one and two dimensions.

a. Close packing in one dimension : A close packed one dimensional structure results by arranging the spheres to touch each other in a row (Fig. 1.3 (a)).

b. Close packing in two dimensions : A close packed two dimensional (planar) structure results by stacking the rows together such

that they are in contact with each other. There are two ways to obtain close packing in two dimensions.

i. Square close packing : One dimensional rows of close packed spheres are stacked over each other such that the spheres align vertically and horizontally (Fig. 1.3 (b)). If the first row is labelled as 'A' type, being exactly same as the first row, the second row is also labelled as 'A' type. Hence this arrangement is called A, A, A, A..... type two dimensional arrangement. In this arrangement, every sphere touches four neighbouring spheres. Hence, two dimensional coordination number, here, is 4. A square is obtained by joining the centres of these four closest neighbours (Fig. 1.3(b)). Therefore, this two dimensional close packing is called **square close packing in two dimension**.

ii. Hexagonal close packing : Close packed one dimensional row (Fig. 1.3 (a)) shows that there are depressions between the neighbouring spheres. If the second row is arranged in such a way that its spheres fit in the depressions of the first row, a staggered arrangement results. If the first row is called 'A' type row, the second row, being different, is called 'B' type. Placing the third row in staggered manner in contact with the second row gives rise to an arrangement in which the spheres in the third row are aligned with the spheres in the first row. Hence the third row is 'A' type. Similarly spheres in the fourth row will be alligned with the spheres in the second row and hence the fourth row would be 'B' type. The resulting two dimensional arrangement is 'ABAB...' type (Fig. 1.3 (c)). In this arrangement each sphere touches six closest neighbours. Thus, the two dimensional coordination number in this packing is 6. A regular hexagon is obtained by joining the centres of these six closest spheres (Fig. 1.3 (c)). Hence, this type of two dimensional close packing is called hexagonal close packing in two dimensions. Compared to the square close packing in two dimensions, the coordination number in hexagonal close packing in two dimensions is higher. Moreover the free space in this arrangement is less than in square packing, making it more efficient packing than square packing. From Fig.1.3(c) it is evident that the free spaces (voids) are triangular in shape. These triangular voids are of two types. Apex of the triangular voids in alternate rows points upwards and downwards.

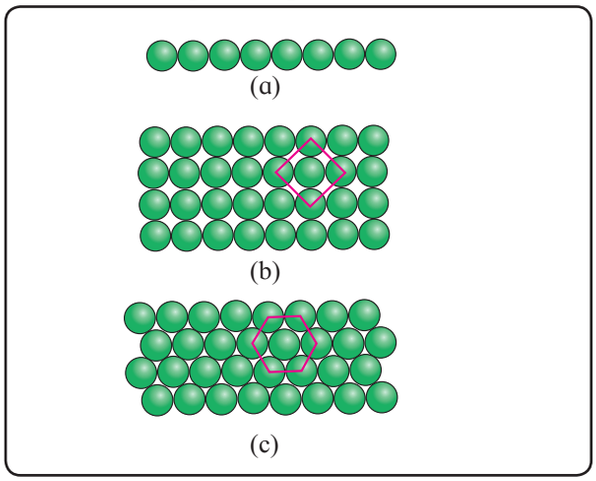


Fig. 1.3 : (a) Close packing in one dimension (b) square close packing (c) Hexagonal close packing in two dimension

c. Close packing in three dimensions : Stacking of two dimensional layers gives rise to three dimensional crystal structures. Two dimensional square close packed layers are found to stack only in one way to give simple cubic lattice. Two dimensional hexagonal close packed layers are found to stack in two distinct ways. Accordingly two crystal structures, namely, hexagonal close packed (hcp) structure and face centred cubic (fcc) structure are formed.

i. Stacking of square close packed layers: Stacking of square close packed layers generates a three dimensional simple cubic structure. Here, the second layer is placed over the first layer so as to have its spheres exactly above those of the first layer (Fig. 1.4). Subsequent square close packed layers are placed one above the other in the same manner. In this arrangement, spheres of all the layers are perfectly aligned horizontally as well as vertically. Hence, all the layers are alike, and are labelled as 'A' layers. This arrangement of layers is described as 'AAAA... ' type. The

structure that results on stacking square close packed layers is **simple cubic**. Its unit cell is the **primitive cubic unit cell** (Fig. 1.4).

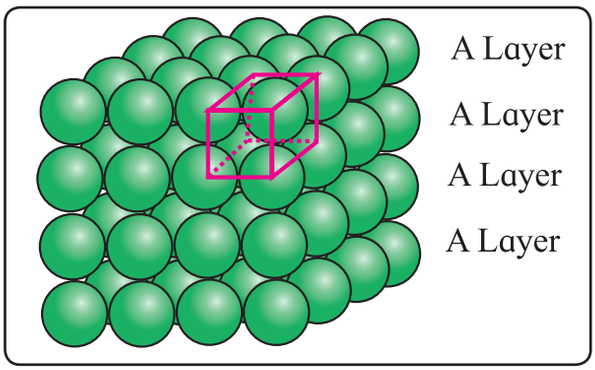


Fig. 1.4 : Stacking of square closed packed layers

It can be seen that in the simple cubic structure, each sphere touches six neighbouring spheres, four in its own layer, one in the layer above and one in the layer below. Hence, coordination number of each sphere is 6. Polonium is the only metal that crystallizes in simple cubic closed packed structure.

ii. Stacking of two hexagonal close packed layers : To generate a close packed three dimensional structure, hexagonal close packed layers are arranged in a particular manner. In doing so, spheres of the second layer are placed in the depression of the first layer (Fig. 1.5). If the first layer is labelled as 'A' layer, the second layer is labelled as 'B' layer because the two layers are aligned differently. It is evident from the Fig. 1.5 that all triangular voids of the first layers are not covered by the spheres of the second layer. The triangular voids that are covered by spheres of the second layer generate tetrahedral void(Fig. 1.6). A tetrahedral void is surrounded by four spheres. On joining the centres of these four spheres a tetrahedron is formed which encloses the tetrahedral voids (Fig. 1.6). The remaining triangular voids of the first layer have above them the triangular voids of the second layer. The overlapping triangular voids from the two layers together form an octahedral void which is surrounded by six spheres (Fig. 1.7).

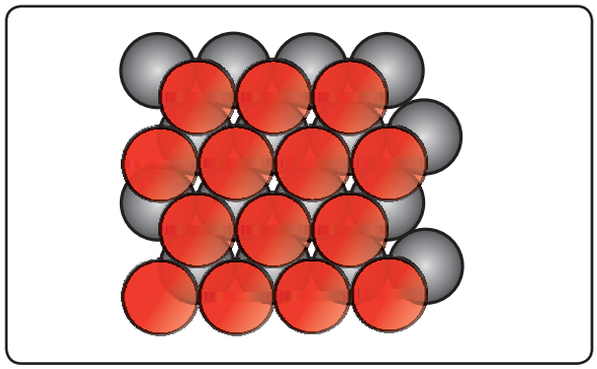


Fig. 1.5 : Two layers of closed packed spheres

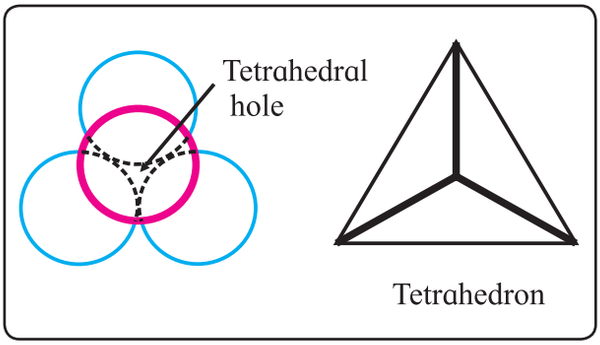


Fig. 1.6 : Tetrahedral void

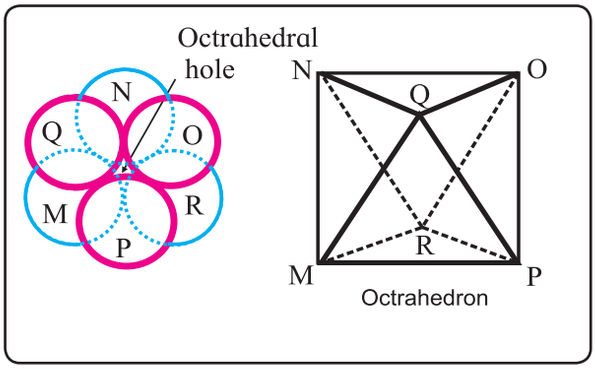


Fig. 1.7 : Octahedral void

Remember...

It is important to note that the triangular shapes of depressions in A and B layer do not overlap. The apices of two triangular depressions in A and B layer point in opposite directions.

The depressions in which spheres of second layer rest are tetrahedral voids while the depressions in which no sphere rests are octahedral voids.

iii. Placing third hexagonal close packed layer : There are two ways of placing the third hexagonal close packed layer on the second.

One way of doing this is to align the spheres of the third layer with the spheres of the first layer. The resulting pattern of the layers will be 'ABAB....'. This arrangement results in **hexagonal close packed (hcp)** structure (Fig. 1.8(a)). Metals such as Mg, Zn, have hcp crystal structure.

The second way of placing the third hexagonal close packed layer on the second is to cover the octahedral voids by spheres of the third layer. In such placing, the spheres of the third layer do not align with the spheres of the second or the spheres of the first layer. The third layer is, therefore, called 'C' layer. The spheres of the fourth layer get aligned with the spheres of the first layer. Hence, the fourth layer is called 'A' layer. This pattern of stacking hexagonal close packed layers is called 'ABCABC....'. This arrangement results **in cubic close packed (ccp)** structure (Fig. 1.8(b)). This is same as fcc structure. Metals such as copper and Ag have ccp (or fcc) crystal structure.

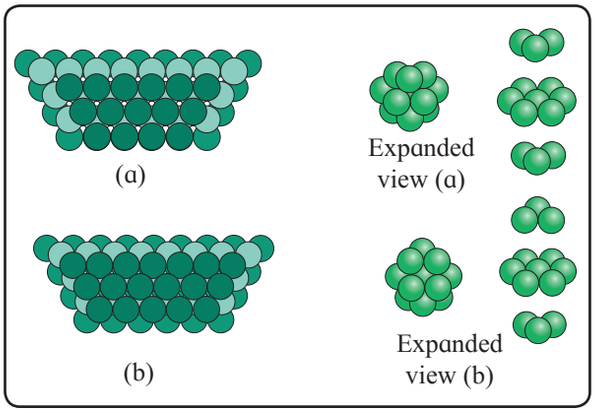


Fig. 1.8 : Formation of hexagonal closed packed structures

1.6.2 Coordination number in close packed structure

a. In the simple cubic (sc) crystal structure, that results from stacking of square close packed layers, each sphere is surrounded by 6 neighbouring spheres, 4 in its own layer, 1 above and 1 below. Hence coordination number of any sphere in sc is 6.

b. In both **hcp** and **ccp/fcc** structures that result from stacking of hexagonal close packed layers in two different ways, each sphere is surrounded by 12 neighbouring spheres, 6 in its own layer, 3 above and 3 below. Hence, the coordination number of any sphere in hcp or ccp/fcc structure is 12.

1.6.3 Number of voids per atom in hcp and ccp : The tetrahedral and octahedral voids occur in hcp and ccp/fcc structures. There are two tetrahedral voids associated with each atom. The number of octahedral voids is half that of tetrahedral voids. Thus, there is one octahedral void per atom.

Remember...

If N denotes number of particles, then number of tetrahedral voids is 2N and that of octahedral voids is N.

1.7 Packing efficiency : Like coordination number, the magnitude of packing efficiency gives a measure of how tightly particles are packed together.

Packing efficiency is the fraction or a percentage of the total space occupied by the spheres (particles).

$$\text{Packing efficiency} = \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100 \quad \ldots\ldots\ldots (1.5)$$

1.7.1 Packing efficiency of metal crystal in simple cubic lattice is obtained by the following steps.

Step 1 : Radius of sphere : In simple cubic unit cell, particles (spheres) are at the corners and touch each other along the edge. A face of simple cubic unit cell is shown in Fig. 1.9. It is evident that

$$a = 2r \quad \text{or} \quad r = a/2 \quad \ldots\ldots\ldots (1.6)$$

where r is the radius of atom and 'a' is the length of unit cell edge.

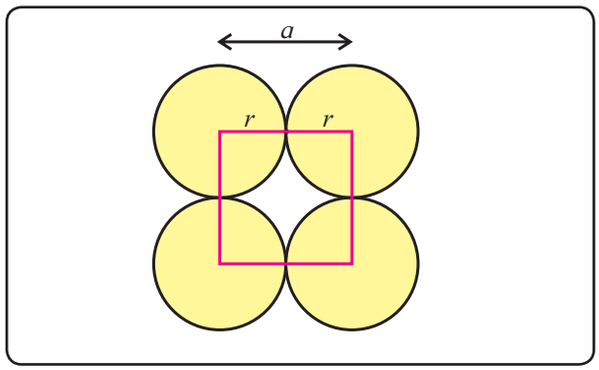


Fig. 1.9 : Face of simple cubic unit cell

Step 2 : Volume of sphere : Volume of a sphere = $(4/3\pi)(r^3)$. Substitution for r from Eq. (1.6) gives

Volume of one particle

$$= (4/3\pi)\,(a/2)^3 = \frac{\pi a^3}{6} \quad \ldots\ldots\ldots (1.7)$$

Step 3 : Total volume of particles : Because simple cubic unit cell contains only one particle,

volume occupied by particle in unit cell $= \frac{\pi a^3}{6}$

Step 4 : Packing efficiency

Packing efficiency

$$= \frac{\text{volume occupied by particle in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\pi a^3/6}{a^3} \times 100 = \frac{100\pi}{6} = \frac{100 \times 3.142}{6} = 52.36\%$$

Thus, in simple cubic lattice, 52.36 % of total space is occupied by particles and 47.64% is empty space, that is, void volume.

1.7.2 Packing efficiency of metal crystal in body-centred cubic lattice

Step 1 : Radius of sphere (particle) :

In bcc unit cell, particles occupy the corners and in addition one particle is at the centre of the cube. Figure 1.10 shows that the particle at the centre of the cube touches two corner particles along the diagonal of the cube. To obtain radius of the particle (sphere) Pythagorus theorem is applied.

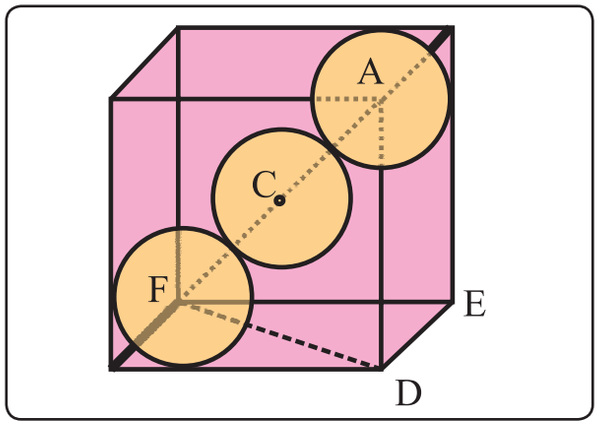


Fig. 1.10 : bcc unit cell

- For triangle FED, $\angle$ FED = 90^0.

$\therefore$ $FD^2 = FE^2 + ED^2 = a^2 + a^2 = 2a^2$ (because FE = ED = a) .....(1.8)

- For triangle AFD, $\angle$ ADF = 90^0

$\therefore$ $AF^2 = AD^2 + FD^2$ .....(1.9)

Substitution of Eq. (1.8) into Eq. (1.9) yields

$AF^2 = a^2 + 2a^2 = 3a^2$ (because AD = a)

or $AF = \sqrt{3}\,a$ .....(1.10)

The Fig. 1.10 shows that AF = $4r$.

Substitution for AF from equation (1.10) gives

$\sqrt{3}a = 4r$ and hence, $r = \frac{\sqrt{3}}{4}\,a$ .....(1.11)

Step 2 : Volume of sphere : Volume of sphere particle = $4/3\ \pi\ r^3$. Substitution for r from Eq. (1.11), gives

volume of one particle $= \frac{4}{3}\,\pi\,(\sqrt{3}/4a)^3$

$$= \frac{4}{3}\,\pi \times \frac{(\sqrt{3})^3}{64}\,a^3$$

$$= \frac{\sqrt{3}\,\pi\,a^3}{16}$$

Step 3 : Total volume of particles : Unit cell bcc contains 2 particles. Hence, volume occupied by particles in bcc unit cell

$$= 2 \times \frac{2\sqrt{3}\,\pi a^3}{16}$$

$$= \frac{\sqrt{3}\,\pi a^3}{8} \quad \ldots\ldots\ldots (1.12)$$

Step 4 : Packing efficiency

Packing efficiency

$$= \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\sqrt{3}\pi a^3}{8a^3} \times 100 = 68\ \%$$

Thus, 68% of the total volume in bcc unit lattice is occupied by atoms and 32 % is empty space or void volume.

1.7.3 Packing efficiency of metal crystal in face-centred cubic lattice (or ccp or hcp lattice)

Step 1 : Radius of particle/sphere : The corner particles are assumed to touch the particle at the centre of face ABCD as shown in Fig. 1.11.

The triangle ABC is right angled with $\angle ABC = 90^0$. According to Pythagorus theorem,

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

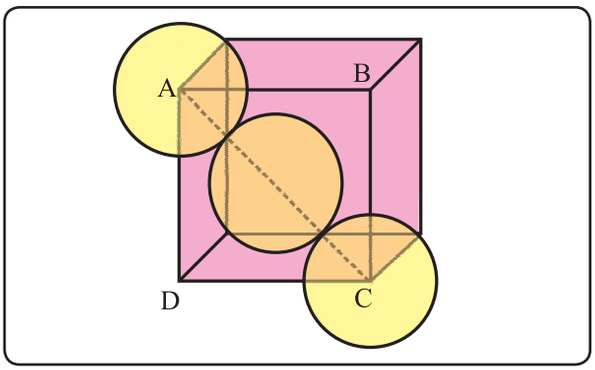


Fig. 1.11 : fcc unit cell

(because AB = BC = a)

Hence, $AC = \sqrt{2}\ a$ ..... (1.13)

Figure 1.11 shows that AC = 4 r. Substitution for AC from Eq. (1.13) gives

$$\sqrt{2}\,a = 4r \text{ or } r = \frac{\sqrt{2}}{4}\,a = \frac{a}{2\sqrt{2}} \quad \text{..... (1.14)}$$

Step 2 : Volume of sphere : Volume of one particle $= \frac{4}{3}\pi r^3$. Substitution for r from Eq. (1.14) gives

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

$$= \frac{4}{3}\pi a^3 \times \left(\frac{1}{2\sqrt{2}}\right)^3$$

$$= \frac{\pi a^3}{12\sqrt{2}}$$

Step 3 : Total volume of particles : The unit cell of fcc lattice contains 4 particles. Hence, volume occupied by particles in fcc unit cell

$$= 4 \times \frac{\pi a^3}{12\sqrt{2}} = \frac{\pi a^3}{3\sqrt{2}}$$

Step 4 : Packing efficiency : Packing efficiency

$$= \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\pi a^3}{3\sqrt{2}a^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$$

Thus in fcc/ccp/hcp crystal lattice, 74% of the total volume is occupied by particles and 26% is void volume or empty space.

Table 1.3 shows the expressions for various parameters of particles in terms of unit cell dimension for cubic systems.

Use your brain power

Which of the three lattices, sc, bcc and fcc has the most efficient packing of particles? Which one has the least efficient packing?

Table 1.3 : Edge length and particle parameters in cubic system

Unit cell	Relation between a and r	Volume of one particle	Total volume occupied by particles in unit cell
1. sc	$r = a/2 = 0.5000a$	$\pi a^3/6 = 0.5237\ a^3$	$\pi a^3/6 = 0.5237\ a^3$
2. bcc	$r = \sqrt{3}a/4 = 0.4330a$	$\sqrt{3}\ \pi a^3/16 = 0.34a^3$	$\sqrt{3}\ \pi a^3/8 = 0.68a^3$
3. fcc/ ccp	$r = \sqrt{2}a/4 = 0.3535a$	$\pi a^3/12\sqrt{2} = 0.185a^3$	$\pi a^3/3\sqrt{2} = 0.74a^3$

Table 1.4 shows the summary of coordination number of particles and packing efficiency in various cubic systems.

Table 1.4 : Coordination number and packing efficiency in systems

Lattice	Coordination number of atoms	Packing efficiency
1. sc	**6 :** four in the same layer, one directly above and one directly below	52.4 %
2. bcc	**8 :** four in the layer below and four in the layer above	68 %
3. fcc/ccp/ hcp	**12 :** six in its own layer, three above and three below	74 %

1.7.4 Number of particles and unit cells in x g of metallic crystal :

The number of particles and the number of unit cells in given mass of a metal can be calculated from the known parameters of unit cell, namely, number of particles 'n' per unit cell and volume 'a^3' of unit cell. Density (ρ) and molar mass (M) of a metal are related to each other through unit cell parameters as shown below :

$$\rho = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{\text{number of particles in unit cell}}{\text{volume of unit cell}} \times \frac{M}{N_A}$$

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

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

where 'n' is the number of particles in unit cell and 'a^3' is the volume of unit cell.

- **Number of particles in 'x' g metal :**

$\because$ Molar mass, M, contains N_A particles

$\therefore$ x g of metal contains $\frac{xN_A}{M}$ particles.

substitution of M gives

$$\text{Number of particles in 'x' g} = \frac{xN_A}{\rho a^3 N_A / n}$$

$$= \frac{xn}{\rho a^3}$$

- **Number of unit cells in 'x' g metal :**

$\because$ 'n' particles correspond to 1 unit cell

$\therefore \frac{xn}{\rho a^3}$ particles correspond to $\frac{xn}{\rho a^3} \times \frac{1}{n}$ unit cells.

$\therefore$ Number of unit cells in 'x' g metal $= \frac{x}{\rho a^3}$

- **Number of unit cells in volume 'V' of metal** $= \frac{V}{a^3}$

Problem 1.2 A compound made of elements C and D crystallizes in fcc structure. Atoms of C are present at the corners of the cube. Atoms of D are at the centres of faces of the cube. What is the formula of the compound?

Solution:

i. C atoms are present at the 8 corners. The contribution of each corner atom to the unit cell is 1/8 atom. Hence, the number of C atom that belongs to the unit cell = 8×(1/8) = 1

ii. D atoms are present at the centres of six faces of unit cell. Each face-centre atom is shared between two cubes. Hence, centribution of each face centre atom to the unit cell is 1/2 atom.

The number of D atoms that belong to unit cell = 1/2×6 =3

There are one C atom and three D atoms in the unit cell.

$\therefore$ Formula of compound = CD_3

Problem 1.3 : The unit cell of metallic silver is fcc. If radius of Ag atom is 144.4 pm, calculate (a) edge length of unit cell(b) volume of Ag atom, (c) the percent of the volume of a unit cell, that is occupied by Ag atoms, (d) the percent of empty space.

Solution:

(a) For fcc unit cell, $r = 0.3535\ a$

$r = 144.4\ pm = 144.4 \times 10^{-12}\ m$

$= 144.4 \times 10^{-10}\ cm$

$$a = \frac{r}{0.3535} = \frac{144.4 \times 10^{-10} cm}{0.3535}$$

$= 4.085 \times 10^{-8}\ cm$

(b) Volume of Ag atom $= \frac{4}{3}\ \pi\ r^3$

$$= \frac{4}{3} \times 3.142 \times (144.4 \times 10^{-10}\ cm)^3$$

$= 1.261 \times 10^{-23}\ cm^3$

(c) In fcc unit cell, there are 4 Ag atoms

Volume occupied by 4 Ag atoms

$= 4 \times 1.26 \times 10^{-23}\ cm^3$

$= 5.044 \times 10^{-23}\ cm^3$

Total volume of unit cell $= a^3$

$= (4.085 \times 10^{-8}\ cm)^3$

$= 6.817 \times 10^{-23}\ cm^3$

Percent of volume occupied by Ag atoms

$$= \frac{\text{volume occupied by atoms in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{5.044 \times 10^{-23} cm^3}{6.817 \times 10^{-23} cm^3} = 74\%$$

(d) Percent empty space = 100 - 74 = 26%

Problem 1.4 : A compound is formed by two elements A and B. The atoms of element B forms ccp structure. The atoms of A occupy 1/3rd of tetrahedral voids. What is the formula of the compound ?

Solution : The atoms of element B form ccp structure. The number of tetrahedral voids generated is twice the number of B atoms.

Thus, number of tetrahedral voids = 2B

The atoms A occupy (1/3) of these tetrahedral voids.

Hence, number of A atoms = 2B×1/3

Ratio of A and B atoms = 2/3 B: 1B

= 2/3:1 = 2:3

Formula of compound = A_2B_3

Problem 1.5 : Niobium forms bcc structure. The density of niobium is 8.55 g/cm^3 and length of unit cell edge is 330.6 pm. How many atoms and unit cells are present in 0.5 g of niobium?

Solution:

i. Number of atoms in x g niobium $= \frac{xn}{\rho a^3}$

x = 0.5 g, $n = 2$ (for bcc structure),

$\rho = 8.55\ g/cm^3$,

$a = 330.6 pm = 3.306 \times 10^{-8} cm$.

Number of atoms in 0.5 g of niobium

$$= \frac{0.5\ g \times 2}{8.55\ g\ cm^{-3} \times (3.306 \times 10^{-8}\ cm)^3}$$

$= 3.25 \times 10^{21}$

ii. Number of unit cells in x g $= \frac{x}{\rho a^3}$

Number of unit cells in 0.5 g of niobium

$$= \frac{0.5\ g \times 2}{8.55\ g\ cm^{-3} \times (3.306 \times 10^{-8} cm)^3}$$

$= 1.62 \times 10^{21}$

Problem 1.6 : A compound forms hcp structure. What is the number of (a) octahedral voids (b) tetrahedral voids (c) total voids formed in 0.4 mol of it.

Solution :

Number of atoms in 0.4 mol = $0.4 \times N_A$

$= 0.4 \times 6.022 \times 10^{23} = 2.4098 \times 10^{23}$

(a) Number of octahedral voids = number of atoms = 2.4098×10^{23}

(b) Number of tetrahedral voids

$= 2 \times$number of atoms

$= 2 \times 2.4098 \times 10^{23}$

$= 4.818 \times 10^{23}$

(c) Total number of voids

$= 2.409 \times 10^{23} + 4.818 \times 10^{23}$

$= 7.227 \times 10^{23}$

1.8 Crystal defects or imperfections : The real, naturally occurring crystalline substances do not have perfect crystal structures. They have some disorders or irregularities in the stacking of atoms. Such irregularities in the arrangement of constituent particles of a solid crystal are called defects or imperfections.

Defects are created during the process of crystallization. The imperfections are more if the crystallization occurs at a faster rate. It means that the defects can be minimized by carrying out crystallization at a slower rate.

In fact ideal crystals with no imperfections are possible only at the absolute zero of temperature. Above this temperature no crystalline materials are 100 % pure. They contain defects.

Whatever be the nature of a crystal defect, electrical neutrality of the solid is maintained.

It is important to note that sometimes defects are to be intentionally created for manipulating the desired properties in crystalline solids.

There are three types of defects: point defects, line defects and plain defects. Only point defects will be discussed in this chapter.

1.8.1 Point defects : These defects are irregularities produced in the arrangement of basis at lattice points in crystalline solids.

There are three major classes of point defects: stoichiometric point defects, impurity defects and nonstoichiometric point defects.

a. Stoichiometric point defects : Chemical formula of a compound shows fixed ratio of number of atoms or number of cations and anions. This fixed ratio is the stoichiometry of the compound.

In stoichiometric defect, the stoichiometry remains unchanged. In other words, the ratio of number of atoms or number of cations and anions of compound remains the same as represented by its chemical formula.

There are four types of stoichiometric point defects: vacancy defect, self interstitial defect, Schottky defect and Frenkel defect.

i. Vacancy defect : During crystallization of a solid, a particle is missing from its regular site in the crystal lattice. The missing particle creates a vacancy in the lattice structure. Thus, some of the lattice sites are vacant because of missing particles as shown in Fig. 1.12. The crystal is, then, said to have a vacancy defect. The vacancy defect can also be developed when the substance is heated.

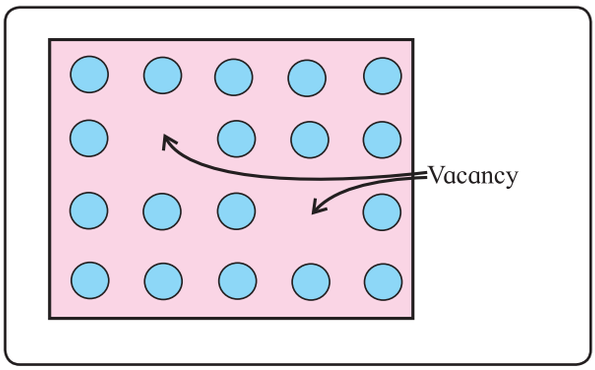


Fig. 1.12 : Vacancy defect

Due to the absence of particles, the mass of the substance decreases. However, the volume remains unchanged. As a result the density of the substance decreases.

ii. Self interstitial defect in elemental solid

Interstitial sites in a crystal are the spaces or voids in between the particles at lattice points. When some particles of a crystalline elemental solid occupy interstitial sites in the crystal structure, it is called self interstitial defect.

This defect occurs in the following two ways :

Firstly, an extra particle occupies an empty interstitial space in the crystal structure as shown in Fig. 1.13. This extra particle is same as those already present at the lattice points.

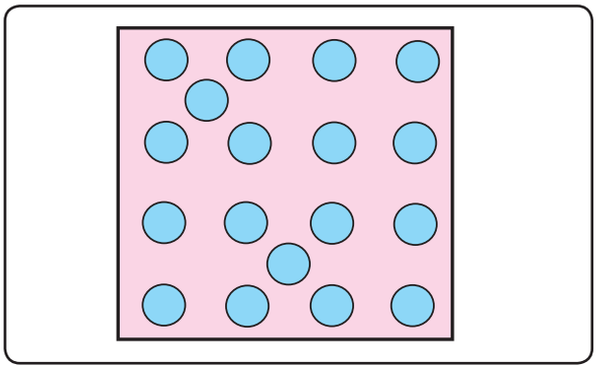


Fig. 1.13 : Self interstitial defect

The extra particles increase the total mass of substance without increasing volume. Hence its density increases.

Secondly, in an elemental solid a particle gets shifted from its original lattice point and occupies an interstitial space in the crystal as shown in the Fig. 1.14.

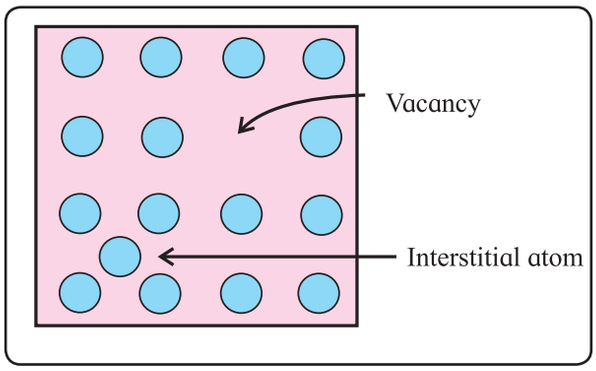


Fig. 1.14 : Self interstitial defect

It is interesting to note that in this second case, because of the displacement of a particle a vacancy defect is created at its original regular lattice site. At the same time interstitial defect results at its new position. We can, therefore, say that in this defect there is a combination of vacancy defect and self interstitial defect.

This defect preserves the density of the substance because there is neither loss nor gain in mass of a substance.

iii. Schottky defect : In an ionic solid, equal number of cations and anions are missing from their regular positions in the crystal lattice creating vacancies as shown in Fig. 1.15. It means that a vacancy created by a loss of cation is always accompanied by a vacancy formed by a loss of anion.

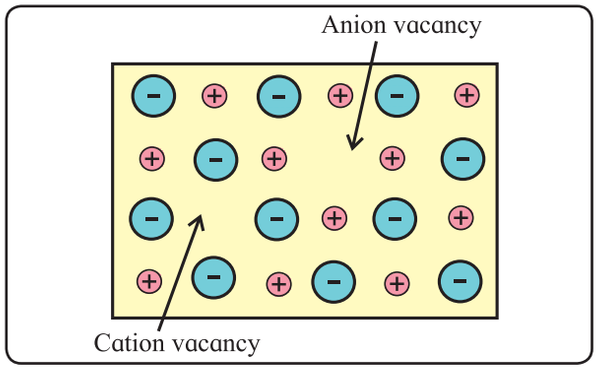


Fig. 1.15 : Schottky defect

Thus, there exist two holes per ion pair lost, one created by missing cation and the other by a missing anion. Such a paired cation-anion vacancy defect is a Schottky defect.

Conditions for the formation of Schottky defect

i. Schottky defect is found in ionic compounds with the following characteristics :

- High degree of ionic character.
- High coordination number of anion
- Small difference between size of cation and anion. The ratio r_{cation}/r_{anion} is not far below unity.

Consequences of Schottky defect

- As the number of ions decreases, mass decreases. However, volume remains unchanged. Hence, the density of a substance decreases.
- The number of missing cations and anions is equal, the electrical neutrality of the compound is preserved.

This defect is found in ionic crystals such as NaCl, AgBr and KCl.

iv. Frenkel defect : Frenkel defect arises when an ion of an ionic compound is missing from its regular lattice site and occupies interstitial position between lattice points as shown in Fig. 1.16.

The cations are usually smaller than anions. It is, therfore, more common to find the cations occupying interstitial sites. It is easier for the smaller cations to accomodate the interstitial spaces.

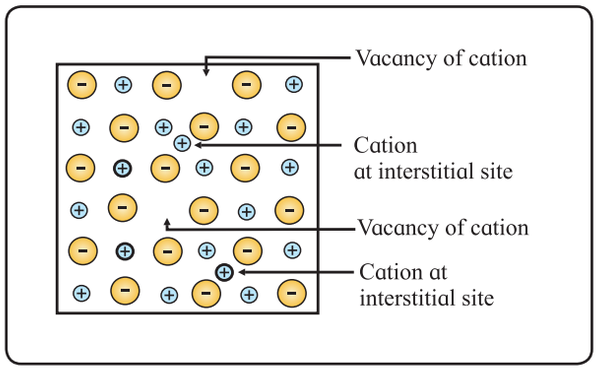


Fig. 1.16 : Frenkel defect

Do you know ?

Frenkel defect is not found in pure alkali metal halides because cations of allkali metals due to large size cannot occupy interstitial space.

It is important to note that the smaller cation is displaced from its normal site to an interstitial space. It, therefore, creates a vacancy defect at its original position and interstitial defect at its new location in the same crystal. Frenkel defect can be regarded as the combination of vacancy defect and interstitial defect.

Conditions for the formation of Frenkel defect

- Frenkel defect occurs in ionic compounds with large difference between sizes of cation and anion.
- The ions of ionic compounds must be having low coordination number.

Consequences of Frenkel defect

- As no ions are missing from the crystal lattice as a whole, the density of solid and its chemical properties remain unchanged.
- The crystal as a whole remains electrically neutral because the equal numbers of cations and anions are present.

This defect is found in ionic crystals like ZnS, AgCl, AgBr, AgI, CaF_2.

b. Impurity defect : Impurity defect arises when foreign atoms, that is, atoms different from the host atoms, are present in the crystal lattice. There are two kinds of impurity defects : Substitutional and interstitial impurity defects.

i. Substitutional impurity defect : In this defect, the foreign atoms are found at the lattice sites in place of host atoms. The regular atoms are displaced from their lattice sites by impurity atoms.

For example :

- **Solid solutions of metals (alloys) :** Brass is an alloy of Cu and Zn. In brass, host Cu atoms are replaced by impurity of Zn atoms. The Zn atoms occupy regular sites of Cu atoms as shown in Fig. 1.17.

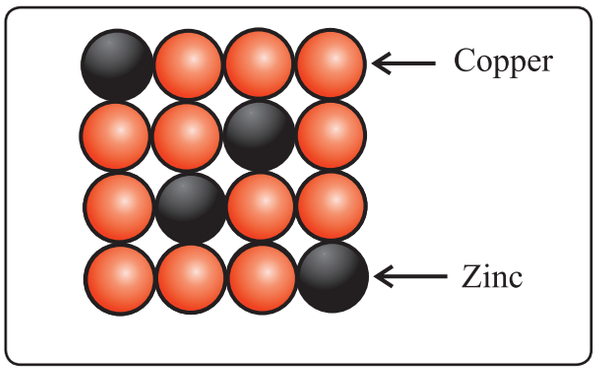


Fig. 1.17 : Brass

- **Vacancy through aliovalent impurity :**

Vacancies are created by the addition of impurities of aliovalent ions (that is, ions with oxidation state (o.s.) different from that of host ions) to an ionic solid.

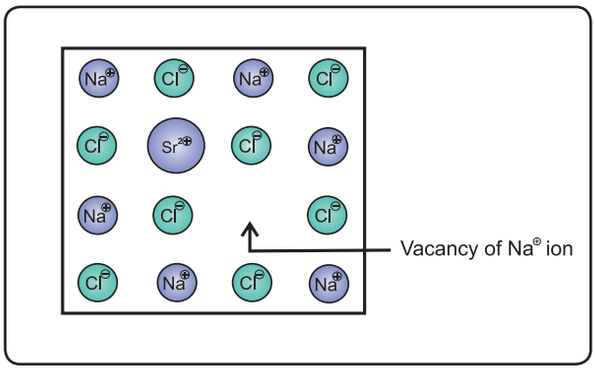


Fig. 1.18 : Vacancy through aliovalent ion

Suppose that a small amount of $SrCl_2$ impurity is added to NaCl during its crystallization. The added $Sr^{2\oplus}$ ions (O.S. + 2) occupy some of the regular sites of $Na^{\oplus}$ host ions (O.S.+1).

In order to maintain electrical neutrality, every $Sr^{2\oplus}$ ion removes two $Na^{\oplus}$ ions. One of the vacant lattice sites created by removal of two $Na^{\oplus}$ ions is occupied by one $Sr^{2\oplus}$ ion. The other site of $Na^{\oplus}$ ion remains vacant as shown in Fig. 1.18.

ii. Interstitial impurity defect : In this defect, the impurity atoms occupy interstitial spaces of lattice structure. For example in steel, Fe atoms occupy normal lattice sites. The carbon atoms are present at interstitial spaces, as shown in Fig. 1.19.

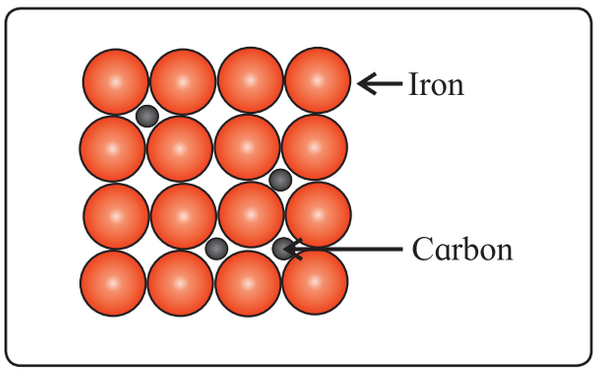


Fig. 1.19 : Stainless steel

c. Nonstoichiometric defects :

Nonstoichiometric defect arises when the ratio of number of atoms of one kind to that of other kind or the ratio of number of cations to anions becomes different from that indicated by its chemical formula. In short, stoichiometry of the compound is changed.

It is important to note that the change in stoichiometry does not cause any change in the crystal structure.

There are two types of nonstoichiometric defects

i. Metal deficiency defect : This defect is possible only in compounds of metals that show variable oxidation states.

In some crystals, positive metal ions are missing from their original lattice sites. The extra negative charge is balanced by the presence of cation of the same metal with higher oxidation state than that of missing cation.

For example, in the compound NiO one $Ni^{2\oplus}$ ion is missing creating a vacnacy at its lattice site. The deficiency of two positive charges is made up by the presence of two $Ni^{3\oplus}$ ions at the other lattice sites of $Ni^{2\oplus}$ ions as shown in Fig. 1.20. The composition of NiO then becomes $Ni_{0.97}O_{1.0}$

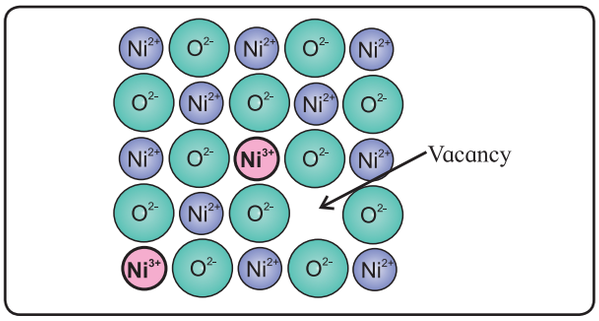


Fig. 1.20 : Nonstoichiometric $Ni_{0.97}O_{1.0}$

ii. Metal excess defect : There are two types of metal excess defects.

- **A neutral atom or an extra positive ion occupies interstitial position :** ZnO presents two ways of metal excess defect. In the first case in ZnO lattice one neutral

Zn atom is present in the interstitial space as shown in Fig. 1.21(a)

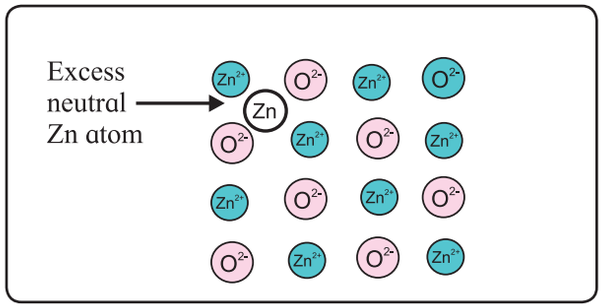


Fig. 1.21 (a) : Neutral Zn atom at interstitial site

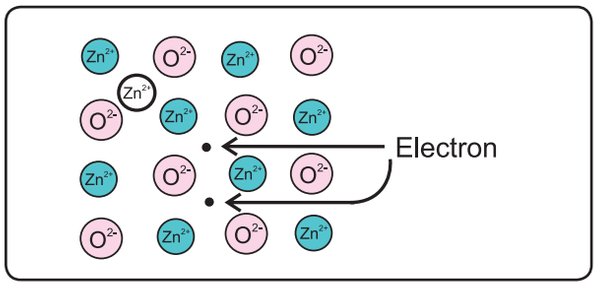


Fig. 1.21 (b) : Zn^{2+} ions and electrons at interestitial sites

In the second case, when ZnO is heated it decomposes as :

$$ZnO \longrightarrow Zn^{2\oplus} + 1/2\ O_2 + 2e^{\ominus}$$

The excess $Zn^{2\oplus}$ ions are trapped in interstitial site in the lattice. The electrons also diffuse in the crystal to occupy interstitial sites as shown in Fig. 1.21(b).

In both the cases, nonstoichiometric formula of ZnO is $Zn_{1+x}O_{1.0}$

Can you think ?

When ZnO is heated it turns yellow and returns back to original white colour on cooling. What could be the reason ?

- **By anion vacancies (Colour or F-centres)**

This type of defect imparts colour to the colourless crystal. For example, when NaCl crystal is heated in the atmosphere of sodium vapour, sodium atoms are deposited on the crystal surface.

$Cl^{\ominus}$ ions diffuse to the crystal surface creating vacancies at their regular sites. These $Cl^{\ominus}$ ions combine with Na atoms on the surface to form NaCl, by releasing electron from sodium atom.

$$Na + Cl^{\ominus} \longrightarrow NaCl + e^{\ominus}$$

The electrons released diffuse into the crystal and occupy vacant sites of anions as shown in Fig. 1.22. The anion vacant sites occupied by electrons are F-centres or colour-centres.

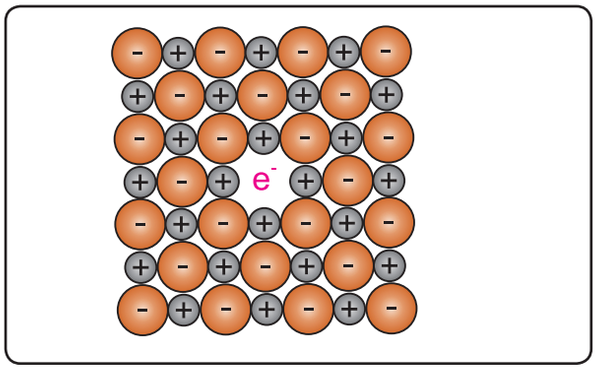


Fig. 1.22 : An F-centre in a crystal

NaCl shows yellow colour due to the formation of F-centre. The crystal of NaCl has excess Na. The nonstoichiometric formula of NaCl is the $Na_{1+x}Cl_{1.0}$

1.9 Electrical properites of solids

Can you recall ?

- What is electrical conductivity ?
- What is meant by the terms electrical 'insulator' and 'semiconductor' ?

Solids show very wide range of electrical conductivity. Accordingly solids are classified into the following three categories : conductors, insulators and semiconductors.

i. Conductors : Solids having electrical conductivities in the range 10^4 to 10^7 $Ohm^{-1}m^{-1}$ are called conductors. Metals and electrolytes (ionic solids) are examples of electrical conductors. Metals conduct electricity by movement of electrons while electrolytes conduct electricity by movement of ions. In

this section we will study some aspects of electronic conduction of electricity.

ii. Insulators : Solids having low electrical conductivities in the range 10^{-20} to 10^{-10} $Ohm^{-1}m^{-1}$ are called insulators. Most nonmetals and molecular solids belong to this category.

iii. Semiconductors : Solids having electrical conductivities in the range 10^{-6} to 10^{4} Ohm^{-1} m^{-1} are semiconductors. This range is intermediate between conductors and insulators. Metalloids like silicon, germanium belong to this category.

1.9.1 Band theory : Electrical conductivities of solid metals, nonmetals and metalloids are explained in terms of band theory. A band is made of closely spaced electronic energy levels. Band formation can be correlated to formation of molecular orbitals (MOs) by interaction of atomic orbitals. (Refer to Std. XI Chemistry Textbook, chapter 5).

Can you recall ?

- How many molecular orbitals are formed by interaction of two atomic orbitals ?
- What is metallic bond ?

According to MO theory interaction of atomic orbitals of combining atoms results in formation of equal number of MOs which spread over the entire molecule. Similar to this, interaction of energy levels of electrons in the closely spaced constituent atoms in solids result in formation of bands. Band theory considers formation of two types of bands, namely, conduction band and valence band. Another important concept of band theory is the band gap.

i. Conduction band : The highest energy band containing electrons is the conduction band. It is formed by interaction of the outermost energy levels of closely spaced atoms in solids. Conduction band may be partially occupied or vacant. Electrons in conduction band are mobile and delocalized over the entire solid. They conduct electricity when electrical potential is applied.

ii. Valence band : The band having lower energy than conduction band is the valence band.

The electrons in valence band are not free to move because they are tightly bound to the respective nuclei.

iii. Band gap : The energy difference between valence band and conduction band is called band gap. Size of the band gap decides whether electrons from valence band can be promoted to vacant conduction band or not when band gap is too large to promote electrons from valence band to vacant conduction band by thermal energy, it is called **forbidden zone**. When band gap is small, electrons from higher energy levels in valence band can be promoted to conduction band by absorption of energy (such as thermal, electromagnetic).

Do you know ?

The band gap energy values of a few solids are as shown here.

Solid	E_{gap} eV
Diamond	5.47
Sodium	0
Silicon	1.12
Germanium	0.67

The electrical properties of metallic conductors, insulators and semiconductors are explained in terms of band theory as follows :

1.9.2 Metals : Metals are good conductors of electricity. The outermost electrons of all the atoms in the metallic crystal occupy conduction band. The number of electrons in conduction band of metals is large. Hence metals are good conductors of electricity. The conduction bands in metals can be further labelled as 's' band (Fig. 1.23 (a)), overlapping s and p bands (Fig. 1.23(b)) and so on. This

depends on the atomic orbitals involved in band formation. Band formation in metallic conductors, thus, results in delocalization of the outermost electrons of all the metal atoms leaving behind metal ions. This is described as 'cations of metal are immersed in the sea of electrons'.

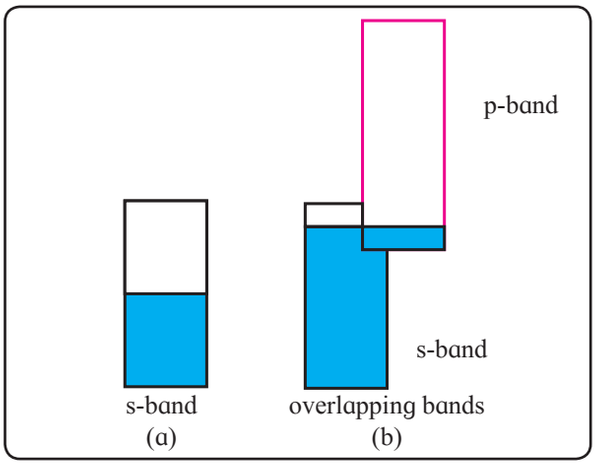


Fig. 1.23: Metalic conductor

The cations of metal atoms occupying lattice sites vibrate about their mean positions. At higher temperatures, metal cations undergo increased vibrational motion about their lattice sites. The flow of electrons is interrupted by increased vibrational motion. As a result conductivity of metals decreases with increase in temperature. (Refer to Std. XI Physics chapter 11).

Do you know ?

- **Metallic sodium** is an example of conductor where the conduction band is partially filled and there is no band gap. Electronic configuration of Na is $[Ar]3s^1$. Interaction of the partially filled 3s AOs of all the Na atoms gives rise to same number of MOs. All these closely spaced MOs together form a continuous band of energies which is called 3s band. Lower half of 3s band corresponds of BMOs and is filled while the upper half of 3s band corresponds to AMOs and is empty. There is no gap between these two halves. The 3s band in sodium is the conduction band which contains same number of electrons as the sodium atoms. This is responsible for the high conductivity of metallic sodium.
- **Metallic magnesium** is an example of conductor with overlapping bands. Electronic configuration of Mg is $[Ar]3s^23p^0$. Interaction of completely filled 3s AOs of all the Mg atoms gives rise to the same number of MOs all of which are filled. These together form the 3s band which is a completely filled band. Interaction of vacant 3p AOs of all the Mg atoms gives rise to the same number of vacant MOs together called 3p band. This is the vacant band. The filled 3s band and vacant 3p band overlap each other. As a result, higher energy electrons move from 3s band to 3p band.

1.9.3 Insulators : In insulators the valence band is completely filled with electrons and the conducation band is empty.

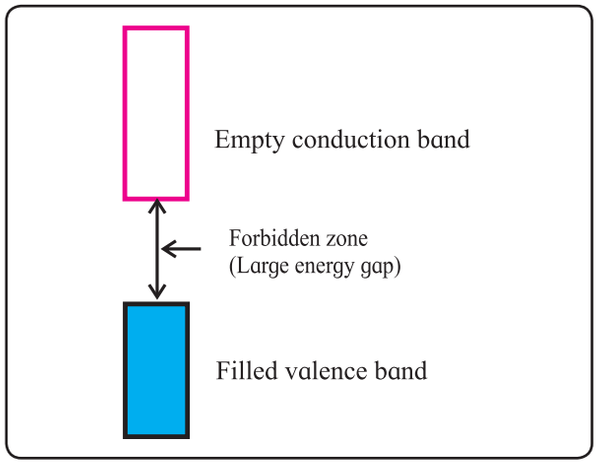


Fig. 1.24: Insulators

The valence band and conduction band in insulators are separated by a large energy gap called forbidden zone as shown in Fig. 1.24. Here, thermal energy is insufficient to promote electrons from valence band to conduction band.

As a result the conduction band remains vacant. The material is, therefore, an insulator.

1.9.4 Semiconductors : Electrical conductivity of a semiconductor material is intermediate between that of metals and insulators. The metalloids Si and Ge are semiconductors.

Like insulators, the valence band in semiconductor is completely filled with electrons and conduction band is empty. However, the energy gap between the two bands is smaller than that in an insulator. (Fig. 1.25)

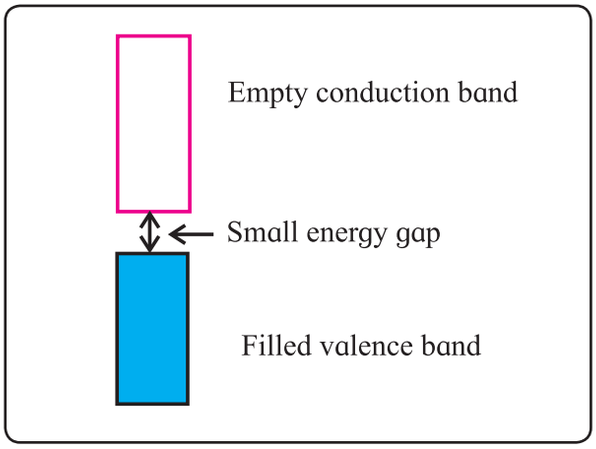


Fig. 1.25 : Semiconductors

At a temperature above absolute zero a few electrons in the valence band have enough thermal energy to jump through the small band gap and occupy higher energy conduction band. The conduction band, thus, becomes partially filled and the valence band becomes partially empty.

The electrons in conduction band are free to move. When electric potential is applied to a semiconductor, it conducts a small amount of electicity.

Such a pure semiconductor material which has a very low but finite electrical conductivity is called **intrinsic semiconductor**.

The electrical conductivity of a semiconductor increases with increasing temperature. This is because, the number of electrons with sufficient energy so as to get promoted to the conduction band increases as temperature rises. Thus, at higher temperatures, there are more mobile electrons in the conduction band and more vacancies in the valence band than at lower temperature. In fact semiconductors are insulators at low temperatures and conductors at high temperatures.

Remember...

Electrical conductivity of metals decreases and that of semiconductor increases with increasing temperature.

1.9.5 Extrinsic semiconductors and doping :

The conductivity of a semiconductor can be increased by doping. The process of addition of minute quantity of impurities to a semiconductor to increase its conductivity is called **doping**. The added impurity is called **dopant**.

A doped semiconductor, having higher conductivity than pure intrinsic semiconductor, is an **extrinsic semiconductor**.

There are two types of extrinsic semiconductors, namely, **n-type** and **p-type** semiconductors.

i. n-type semiconductor : n-type semiconductor contains increased number of electrons in the conduction bond.

An n-type semiconductor is obtained by adding group 15 element to intrinsic semiconductor which belongs to group 14.

Can you tell ?

Let a small quantity of phosphorus be doped into pure silicon.

- Will the resulting material contain the same number of total number of electrons as the original pure silicon ?
- Will the material be electrically neutral or charged ?

Consider, for example, doping of Si with phosphorus. Si has a crystal structure in which each Si atom is linked tetrahedrally to four other Si atoms. When small quantity of

phosphorous is added to pure Si, the P atoms occupy some vacant sites in the lattice in place of Si atoms, as shown in Fig. 1.26. The overall crystal structure of Si remains unchanged.

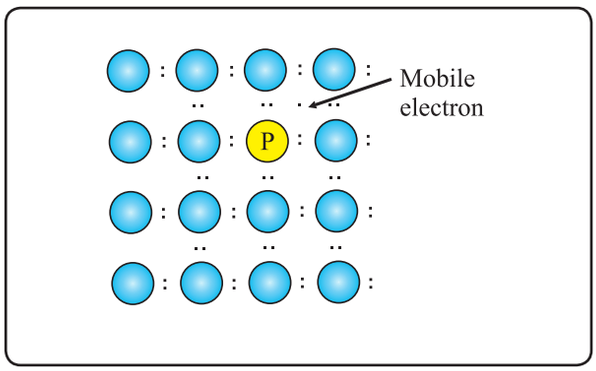


Fig. 1.26 : P atom occupying regular site of Si atom

Four of the five valence electrons of P are utilized in bonding the closest to four Si atoms. Thus, P has one extra electron than needed for bonding. Therefore, Si doped with P has more number of electrons in the conduction band than those in the conduction band in pure Si as shown in Fig. 1.27. It is thus transperent that the conductivity of Si doped with P is higher than that of pure Si. The electrons in conduction band move under the influence of an applied potential and conduct electricity.

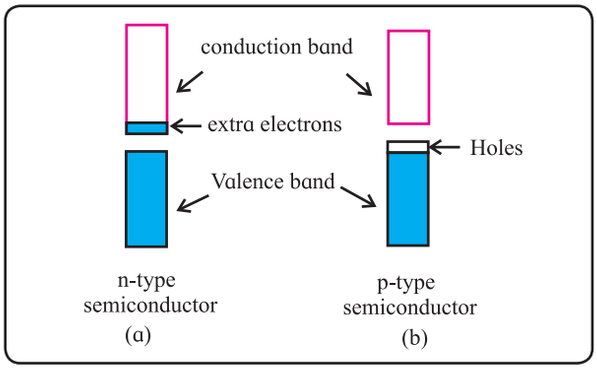


Fig. 1.27 : n-type and p-type semiconductor

Because the charge carriers are the increased number of electrons, Si or Ge doped with group 15 elements such as P, As, Sb or Bi is an n-type semiconductor.

ii. p-type semiconductor : A p-type semiconductor is produced by doping a pure semiconductor material (Si or Ge) with an impurity of group 13 elements. These elements contain less number of valence electrons than that of the pure semiconductor.

Consider, for example, pure Si doped with boron. The B atoms occupy normal positions of some of the Si atoms in the lattice as shown in Fig. 1.28. Boron atom has only three valence electrons. It does not have enough electrons to form bonds with its four Si neighbours.

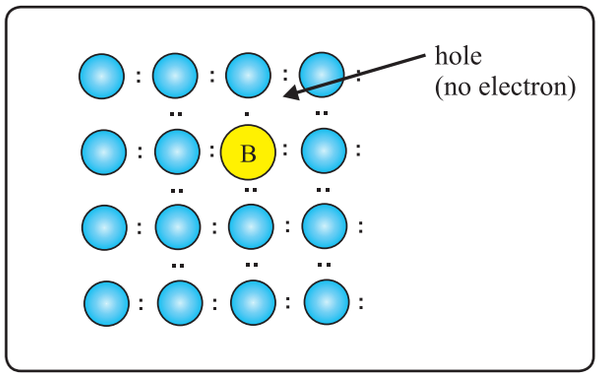


Fig. 1.28 : B atom occupying regular site of Si atom

B atom forms bonds with three Si atoms only. The missing fourth electron creates an electron vacancy. It is called a **hole**.

Fig. 1.28 shows the holes in the valence band of p-type semiconductor.

A hole has a tendency to accept electron from its close vicinity. Thus, a hole behaves as if it has a positive charge. The electrons in partially filled valence band move under the influence of an applied potential. The holes move in the opposite direction.

Remember...

- Whether intrinsic or extrinsic semiconductor, the material is electrically neutral.
- An n-type semiconductor such as Si doped with P has more electrons than those needed for bonding and thus has electrons in the partially filled conduction band.
- A p-type semiconductor such as Si doped with B has the less electrons than needed for bonding and thus has vacancies (holes) in the valence band.

Because the charge carriers are holes which behave like positive charge, the Si or Ge doped with group 13 elements like B, Ga or In, is a p-type semiconductor.

1.10 Magnetic properties of solids : Magnetic properties of solids can be understood easily in terms of classical picture of electron. The electrons spin about their own axis. The spinning electrons act like tiny magnets because their spinning action generates induced magnetic field.

If an orbital contains one electron, the unbalanced spin exhibits magnetism. However, when electrons are paired their spin is balanced and no magnetic property is observed. On the basis of magnetic properties solids are classified into three major classes : diamagnetic, paramagnetic and ferromagnetic.

i. Diamagnetic solids : The substances with all electrons paired, are weakly repelled by magnetic fields. These substances are said to be diamagnetic.

Pairing of electrons balances the spins and hence, cancels their magnetic moments.

N_2, F_2, NaCl, H_2O and benzene are some examples of diamagnetic substances.

ii. Paramagnetic solids : The substances with unpaired electrons are weakly attracted by magnetic field. These substances are called paramagnetic substances.

The spinning of unpaired electron gives rise to a magnetic moment. The substance is attracted by magnetic field because of magnetic moment. It is important to understand that these substances exhibit magnetism in presence of external magnetic field only. They lose magnetism when the external magnetic field is removed.

Oxygen, $Cu^{2\oplus}$, $Fe^{3\oplus}$, $Cr^{3\oplus}$ are some examples of paramagnetic substances.

iii. Ferromagnetism : The substances containing large number of unpaired electrons are attracted strongly by magnetic field. These substances are said to be ferromagnetic.

These substances can be permanently magnetised. They retain magnetism even after the removal of external magnetic field.

Some example of ferromagnetic substances are Fe, Co, Ni, Gd, CrO_2.

Exercises

1. Choose the most correct answer.

i. Molecular solids are
   a. crystalline solids
   b. amorphous solids
   c. ionic solids
   d. metallic solids

ii. Which of the follwong is n-type semiconductor?
   a. Pure Si
   b. Si doped with As
   c. Si doped with Ga
   d. Ge doped with In

iii. In Frenkel defect
   a. electrical neutrality of the substance is changed.
   b. density of the substance is changed.
   c. both cation and anion are missing
   d. overall electical neutrality is preserved.

iv. In crystal lattice formed by bcc unit cell the void volume is
   a. 68 % b. 74 %
   c.32 % d. 26 %

v. The coordination number of atoms in bcc crystal lattice is

a. 2 b. 4

c. 6 d. 8

vi. Which of the following is not correct?

a. Four spheres are involved in the formation of tetrahedral void.

b. The centres of spheres in octahedral voids are at the apices of a regular tetrahedron.

c. If the number of atoms is N the number of octahedral voids is 2N.

d. If the number of atoms is N/2, the number of tetrahedral voids is N.

vii. A compound forms hcp structure. Number of octahedral and tetrhedral voids in 0.5 mole of substance is respectively

a. 3.011×10^{23}, 6.022×10^{23}

b. 6.022×10^{23}, 3.011×10^{23}

c. 4.011×10^{23}, 2.011×10^{23}

d. 6.011×10^{23}, 12.022×10^{23}

vii. Pb has fcc structure with edge length of unit cell 495 pm. Radius of Pb atom is

a. 205 pm b. 185 pm

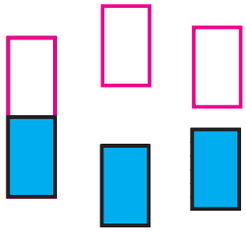
c. 260 pm d. 175 pm

2. Answer the following in one or two sentences

i. What are the types of particles in each of the four main classes of crystalline solids ?

ii. Which of the three types of packing used by metals makes the most efficient use of space and which makes the least efficient use?

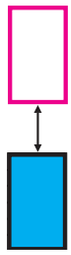
iii. The following pictures show population of bands for materials having different electrical properties. Classify them as insulator, semiconductor or a metal.



iv. What is the unit cell?

v. How does electrical conductivity of a semiconductor change with temperature? Why?

vi. The picture represents bands of MOs for Si. Label valence band, conduction band and band gap.



vii. A solid is hard, brittle and electrically nonconductor. Its melt conducts electricity. What type of solid is it?

viii. Mention two properties that are common to both hcp and ccp lattices.

ix. Sketch a tetrahedral void.

x. What are ferromagnetic substances?

3. Answer the following in brief.

i. What are valence band and conduction band?

ii. Distinguish between ionic solids and molecular solids.

iii. Calculate the number of atoms in fcc unit cell.

iv. How are the spheres arranged in first layer of simple cubic close-packed structures? How are the successive

layers of spheres placed above this layer?

v. Calculate the packing efficiency of metal crystal that has simple cubic structure.

vi. What are paramagnetic substances? Give examples.

vii. What are the consequences of Schottky defect?

viii. Cesium chloride crystallizes in cubic unit cell with $Cl^{\ominus}$ ions at the corners and a $Cs^{\oplus}$ ion in the centre of the cube. How many CsCl molecules are there in the unit cell?

ix. Cu crystallizes in fcc unit cell with edge length of 495 pm. What is the radius of Cu atom?

x. Obtain the relationship between density of a substance and the edge length of unit cell.

4. The density of iridium is 22.4 g/cm^3. The unit cell of iridium is fcc. Calculate the radius of iridium atom. Molar mass of iridium is 192.2 g/mol. (136 pm)

5. Aluminium crystallizes in cubic close packed structure with unit cell edge length of 353.6 pm. What is the radius of Al atom? How many unit cells are there in 1.00 cm^3 of Al? (125 pm, 2.26×10^{22})

6. In an ionic crystalline solid atoms of element Y form hcp lattice. The atoms of element X occupy one third of tetrahedral voids. What is the formula of the compound ? (X_2Y_3)

7. How are tetrahedral and octahedral voids formed?

8. Third layer of spheres is added to second layer so as to form hcp or ccp structure. What is the difference between the addition of third layer to form these hexagonal close-packed structures?

9. An element with molar mass 27 g/mol forms cubic unit cell with edge length of 405 pm. If density of the element is 2.7 g/cm^3. What is the nature of cubic unit cell? (fcc or ccp)

10. An element has a bcc structure with unit cell edge length of 288 pm. How many unit cells and number of atoms are present in 200 g of the element? (1.16×10^{24}, 2.32×10^{24})

11. Distinguish with the help of diagrams metal conductors, insulators and semiconductors from each other.

12. What are n-type semiconductors? Why is the conductivity of doped n-type semiconductor higher than that of pure semiconductor? Explain with diagram.

13. Explain with diagram, Frenkel defect. What are the conditions for its formation? What is its effect on density and electrical neutrality of the crystal?

14. What is an impurity defect? What are its types? Explain the formation of vacancies through aliovalent impurity with example.

Activity :

- **With the help of plastic balls, prepare models of**
  1. **tetrahedral and octahedral voids.**
  2. **simple cubic, bcc and fcc unit cells.**
  3. **ccp and hcp lattices.**
- **Draw structures of network of carbon atoms in diamond and graphite. Discuss with reference to the following points :**
  1. **Are the outermost electrons of carbons in diamond localized or delocalized ?**
  2. **Is the energy gap between BMOs and AMOs in diamond expected to be large or small ?**

2. SOLUTIONS

2.1 Introduction

You are familiar with mixtures. The mixture is a combination of two or more substances. Air is a mixture of gases, rock is a mixture of two or more minerals and so forth.

Recall that the mixtures are (a) homogeneous in which mixing of components is uniform or (b) heterogeneous which have nonuniform mixing of components.

We studied in standard XI, that homogeneous mixtures are classified according to the size of their constituent particles as colloids or as true solutions. In this chapter we deal with the properties of homogeneous mixtures especially of true solutions.

Can you recall ?
The size of particles of colloids and those of true solutions.

The solutions are commonly found in all life processes. The body fluids are solutions. The solutions are also important for industrial processes, and many other areas.

Can you recall ?
The terms solute and solvent.

The solution is a homogeneous mixture of two or more pure substances. A true solution consists of a solvent and one or more solutes. We explore the properties of binary true solutions containing only one solute.

2.2 Types of solutions

We generally think that a solution is a either solid dissolved in liquid or a mixture of two liquids. There are other types of solutions as well. The solute and the solvent may be in any of three states namely, solid, liquid or gas. The solutions thus may involve any combination of these three states of their components. This gives rise to nine types of solutions depending on the states of solute and solvent. These are summarised in table 2.1.

Table 2.1 : Types of solutions

No.	State of solute	State of solvent	Some examples
1	Solid	Liquid	Sea water, benzoic acid in benzene, sugar in water
2	Solid	Solid	Metal alloys such as brass, bronze.
3	Solid	Gas	Iodine in air
4	Liquid	Liquid	Gasoline, ethanol in water.
5	Liquid	Solid	Amalgams of mercury with metals as mercury in silver
6	Liquid	Gas	Chloroform in nitrogen
7	Gas	Liquid	Carbonated water (CO_2 in water), oxygen in water.
8	Gas	Solid	H_2 in palladium
9	Gas	Gas	Air (O_2, N_2, Ar and other gases)

Our focus, in this chapter, will be on the solution of solid in liquid with some attention to a solution of gas in liquid. The solvent in most of the cases will be water.

Can you recall ?
The different units used to express the concentrations of solutions.

2.3 Capacity of solution to dissolve solute

Chemists need to know the capacity of solutions to dissolve a solute. Suppose that a solute is added to a solvent. It dissolves readily at first. The dissolution then slows down as more solute is added. If we continue the

addition of solute, the dissolution stops. The solution at this point is said to be saturated. A dynamic equilibrium can be reached where the number of solute molecules leaving the crystal to pass into solution is equal to the number returning from the solution to the crystal. Thus,

$$\text{Solute} + \text{solvent} \underset{\text{crystallization}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{Solution}$$

A saturated solution contains maximum amount of solute dissolved in a given amount of solvent at a given temperature. A solution containing greater than the equilibrium amount of solute is said to be supersaturated solution. Such solutions are unstable. The precipitation occurs by the addition of a tiny crystal of solute and the supersaturated solution changes to saturated solution.

2.4 Solubility : The solubility of a solute is its amount per unit volume of saturated solution at a specific temperature. The solubility of a solute is its maximum concentration and expressed in the concentration units mol L^{-1}.

2.4.1 Factors affecting solubility : The extent to which a substance dissolves in a solvent varies greatly with different substances. It depends on the nature of solute and solvent, temperature and pressure.

i. Nature of solute and solvent : Generally the compounds with similar chemical character are more readily soluble in each other than those with entirely different chemical characters. The saying that 'like dissolves like' guides to predict the solubility of a solute in a given solvent.

Thus, substances having similar intermolecular forces are likely to be soluble in each other. Generally polar solutes dissolve in polar solvents. This is because in these, solute-solute, solute-solvent and solvent-solvent interactions are all of similar magnitude. For example, NaCl dissolves in water. The strong ion-dipole interactions of $Na^{\oplus}$ and $Cl^{\ominus}$ ions with water molecules, hydrogen bonding between water molecules and ion-ion attractions between $Na^{\oplus}$ and $Cl^{\ominus}$ ions are comparable.

Can you recall ?

The types of force between molecules.

Nonpolar organic compounds like cholesterol dissolves in nonpolar solvent such as benzene.

Can you tell ?

Why naphthalene dissolves in benzene but not in water?

Sugar dissolves in water! The dissolution of sugar in water is due to intermolecular hydrogen bonding between sugar and water.

ii. Effect of temperatute on solubility : How solubility of substance changes with temperature depends on enthalpy of solution. Many solids, for example KCl, dissolve in water by endothermic process, that is, with the absorption of heat. When temperature is increased by adding heat to the system, the solubility of substance increases according to the Le-Chatelier principle. Addition of heat causes a stress on the saturated solution. This stress favours endothermic process.

Can you recall ?

Le-Chatelier principle, exothermic and endothermic processes.

On the other hand, when the substance dissolves in water by an exothermic process its solubility decreases with an increase of temperature. The substances such as $CaCl_2$ and $Li_2SO_4.H_2O$ dissolve in water releasing heat.

Can you tell ?

Anhydrous sodium sulphate dissolves in water with the evolution of heat. What is the effect of temperature on its solubility ?

It is important to understand that there is no direct correlation between solubility and exothermicity or endothermicity. For example, dissolution of $CaCl_2$ in water is exothermic and that of NH_4NO_3 is endothermic. The solubility of these increases with the temperature.

Figure 2.1 shows the result of experimental determination of solubilities of some ionic solids in water at various temperatures. Following are some experimental observations from Fig 2.1

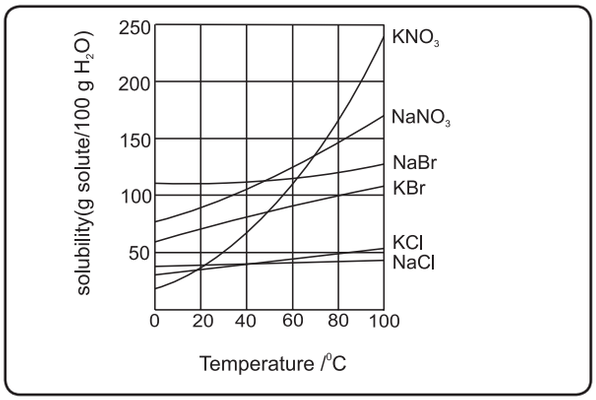


Fig. 2.1 : Variation of solubilities of some ionic solids with temperature

i. Solubilities of NaBr, NaCl and KCl change slightly with temperature.

ii. Solubilities of KNO_3, $NaNO_3$ and KBr increase appreciably with increasing temperature.

iii. Solubility of Na_2SO_4 decreases with increase of temperature.

The solubility of gases in water usually decreases with increase of temperature. When gases are dissolved in water, the gas molecules in liquid phase are condensed. The condensation is an exothermic process. The solubility of gases in water must decrease as temperature is raised.

In united states about 1000000 billion galons of water from rivers and lakes are used for industrial cooling. The cooling process heats water. The hot water then returns to rivers and lakes. The solubility of oxygen decreases in hot water thereby affecting the life of cold blooded animals like fish.

iii. Effect of pressure on solubility

Pressure has no effect on the solubilities of solids and liquids as they are incompressible. However pressure greatly affects solubility of gases in liquids. The solubility of gases increases with increasing pressure. The quantitative relationship between gas solubility in a liquid and pressure is given by Henry's law.

Henry's law: It states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. Thus,

$$S \propto P \text{ or } S = K_H P \qquad \ldots\ldots\ldots (2.1)$$

where, S is the solubility of the gas in mol L^{-1}, P is the pressure of the gas in bar over the solution. K_H, the proportionality constant is called Henry's law constant.

$$\text{Units of } K_H : K_H = \frac{S}{P} = \frac{\text{mol } L^{-1}}{\text{bar}}$$
$$= \text{mol } L^{-1} \text{ bar}^{-1}$$

When P = 1 bar, $K_H = S$. Thus, K_H is the solubility of the gas in a liquid when its pressure over the solution is 1 bar.

Demonstration of Henry's law.

Before sealing the bottle of soft drink, it is pressurised with a mixture of air, CO_2 saturated with water vapour. Because of high partial pressure of CO_2, its amount dissolved in soft drink is higher than the solubility of CO_2 under normal conditions.

When the bottle of soft drink is opened, excess dissolved CO_2 comes out with effervescence.

Exceptions to Henry's law

Gases like NH_3 and CO_2 do not obey Henry's law. The reason is that these gases react with water.

$$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$
$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Because of these reactions, NH_3 and CO_2 gases have higher solubilities than expected by Henry's law.

Do you know ?

O_2 gas has very low solubility in water. However, its solubility in blood is exceedingly high. This is because of binding of O_2 molecule to haemoglobin present in blood.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

Problem 2.1 : The solubility of N_2 gas in water at 25 ^{0}C and 1 bar is 6.85×10^{-4} mol L^{-1}. Calculate (a) Henry's law constant (b) molarity of N_2 gas dissolved in water under atmospheric conditions when partial pressure of N_2 in atmosphere is 0.75 bar.

Solution :

a. $K_H = \frac{S}{P} = \frac{6.85 \times 10^{-4} \text{ mol dm}^{-3}}{1 \text{ bar}}$

$= 6.85 \times 10^{-4}$ mol L^{-1} bar^{-1}

b. $S = K_H P = 6.85 \times 10^{-4}$ mol L^{-1} bar^{-1} $\times$ 0.75 bar

$= 5.138 \times 10^{-4}$ mol L^{-1}

Problem 2.2 : The Henry's law constant of methyl bromide (CH_3Br), is 0.159 mol L^{-1} bar^{-1} at 25^{0}C. What is the solubility of methyl bromide in water at 25^{0}C and at pressure of 130 mmHg?

Solution :

According to Henry's law

$$S = K_H P$$

1. $K_H = 0.159$ mol L^{-1} bar^{-1}

2. $P = 130 \text{ mm Hg} \times \frac{1}{760 \text{ mm Hg/atm}}$

$= 0.171 \text{ atm} \times 1.013 \text{ bar/atm}$

$= 0.173$ bar

Hence, $S = 0.159$ mol L^{-1} bar^{-1} $\times$ 0.173 bar

$= 0.0275$ M

2.5 Vapour pressure of solutions of liquids in liquids : Consider a binary solution of two volatile liquids A_1 and A_2. When the solution is placed in a closed container, both the liquids vaporize. Eventually an equilibrium is established between vapor and liquid phases. Both the components are present in the vapour phase. The partial pressure of the components are related to their mole fractions in the solution. This realationship is given by Raoult's law.

2.5.1 Raoult's law : It states that the partial vapour pressure of any volatile component of a solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.

Suppose that for a binary solution of two volatile liquids A_1 and A_2, P_1 and P_2 are their partial vapour pressures and x_1 and x_2 are their mole fractions in solution. Then according to Raoult's law,

we write $P_1 = x_1 P_1^0$ and $P_2 = x_2 P_2^0$ ..... (2.2)

where P_1^0 and P_2^0 are vapour pressures of pure liquids A_1 and A_2, respectively.

According to Dalton's law of partial pressures, the total pressure P above the solution is,

$$P = P_1 + P_2$$

$$= P_1^0 x_1 + P_2^0 x_2 \quad \text{..... (2.3)}$$

Since $x_1 = 1 - x_2$, the Eq. (2.2) can also be written as

$$P = P_1^0 (1-x_2) + P_2^0 x_2$$

$$= P_1^0 - P_1^0 x_2 + P_2^0 x_2$$

$$= (P_2^0 - P_1^0) x_2 + P_1^0 \quad \text{..... (2.4)}$$

Because P_1^0 and P_2^0 are constants, a plot of P versus x_2 is a straight line as shown in the Fig 2.2. The figure also shows the plots of P_1 versus x_1 and P_2 versus x_2 according to the equations 2.2. These are straight lines passing through origin.

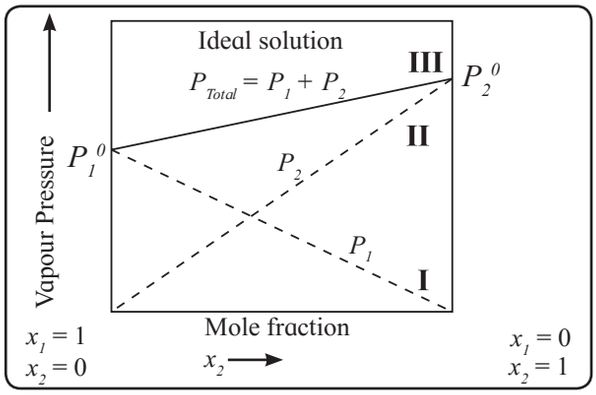


Fig. 2.2 : Variation of vapour pressure with mole fraction of solute

i. For P versus x_2 straight line,

$P = P_1^0$ at $x_2 = 0$ and $P = P_2^0$ at $x_2 = 1$

ii. For P_1 versus x_1 straight line,

$P_1 = 0$ at $x_1 = 0$ and $P_1 = P_1^0$, at $x_1 = 1$

iii. For P_2 versus x_2 straight line,

$P_2 = 0$ at $x_2 = 0$ and $P_2 = P_2^0$ at $x_2 = 1$

Composition of vapour phase :

The composition of vapour in equilibrium with the solution can be determined by Dalton's law of partial pressures.

If we take y_1 and y_2 as the mole fractions of two components in the vapour, then $P_1 = y_1P$ and $P_2 = y_2P$

where P_1 and P_2 are the partial pressures of two components in the vapour and P is the total vapour pressure.

Problem 2.3 : The vapour pressures of pure liquids A and B are 450 mm Hg and 700 mm Hg, respectively at 350 K. Find the composition of liquid and vapour if total vapour pressure is 600 mm.

Solution : i. Compositions of A and B in the solution are x_1 and x_2

$$P = (P_2^0 - P_1^0)\, x_2 + P_1^0$$

$P_1^0 = 450$ mmHg, $P_2^0 = 700$ mmHg,

$P = 600$ mmHg

Hence, 600 mm Hg = (700 mm Hg - 450 mm Hg)x_2 + 450 mm Hg

$= 250x_2 + 450$

$600 - 450 = 150 = 250x_2$ or $x_2 = \frac{150}{250} = 0.6$

$x_1 = 1 - x_2 = 1 - 0.6 = 0.4$

ii. Compositions of A and B in vapour are y_1 and y_2 respectively.

$P_1 = y_1P$ and $P_2 = y_2P$, $P_1 = P_1^0x_1$ and

$P_2 = P_2^0x_2$

$$y_1 = \frac{P_1}{P} = \frac{P_1^0x_1}{P} = \frac{450 \text{ mm Hg} \times 0.4}{600 \text{ mmHg}}$$

$= 0.3$

$y_2 = 1 - y_1 = 1 - 0.3 = 0.7$

2.5.2 Ideal and nonideal solutions

1. Ideal solutions

i. Ideal solutions obey Raoult's law over entire range of concentrations.

ii. No heat is evolved or absorbed when two components forming an ideal solution are mixed. Thus, the enthalpy of mixing is zero. $\Delta_{mix}H = 0$

iii. There is no volume change when two components forming an ideal solution are mixed. Thus volume of an ideal solution is equal to the sum of volumes of two components taken for mixing.

$\Delta_{mix}V = 0$

iv. In an ideal solution solvent-solute, solute-solute and solvent-solvent molecular interactions are comparable.

v. The vapour pressure of ideal solution always lies between vapour pressures of pure components, as shown in Fig. 2.2.

It is important to understand that perfectly ideal solutions are uncommon and solutions such as benzene + toluene behave nearly ideal.

2. Nonideal solutions

i. These solutions do not obey Raoult's law over the entire range of concentrations.

ii. The vapour pressures of these solutions can be higher or lower than those of pure components.

iii. Deviation from the Raoult's law : These solutions show two types of deviation from the Raoult's law.

A. Positive deviations from Raoult's law -

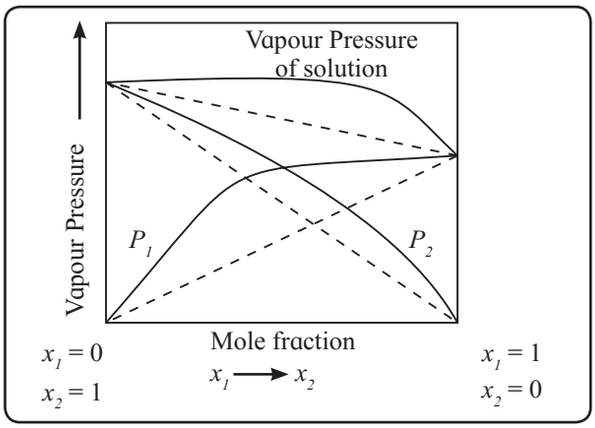


Fig. 2.3 : Positive derivations from Raoult's law

The solutions in which solute-solvent intermolecular attractions are weaker than those between solute-solute molecules and solvent-solvent molecules, exhibit positive deviations. The vapour pressures of such solutions are higher than those of pure components as shown in Fig. 2.3. The solutions of ethanol and acetone, carbon disulphide and acetone show positive deviations from the Raoult's law.

B. Negative deviations from Raoult's law

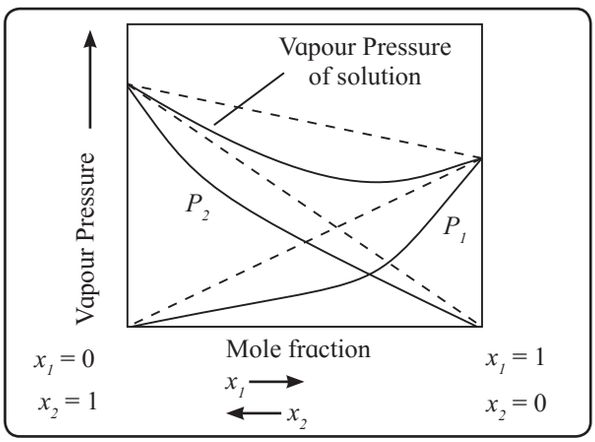


Fig. 2.4 : Negative derivations from Raoult's law

The solutions in which the interactions between solvents and solute molecules are stronger than solute-solute or solvent-solvent interactions, exhibit negative deviations.The vapour pressures of such solutions are lower than those of pure components as shown in Fig. 2.4. The solutions of phenol and aniline, chloroform and acetone exhibit negative deviations from the Raoult's law.

2.6 Colligative properties of nonelectrolyte solutions : The physical properties of solutions that depend on the number of solute particles in solutions and not on their nature are called colligative properties. These are

1. vapour pressure lowering
2. boiling point elevation
3. freezing point depression
4. osmotic pressure

While dealing with colligative properties of nonelectrolyte solutions, the relatively dilute solutions with concentrations 0.2 M or less are considered.

2.7 Vapour pressure lowering : When a liquid in a closed container is in equilibrium with its vapours, the pressure exerted by the vapour on the liquid is its vapour pressure.

Can you recall ?

Vapour pressure of a liquid

i. Experiments have shown that when a nonvolatile, nonionizable solid is dissolved in a liquid solvent, the vapour pressure of the solution is lower than that of pure solvent. In other words the vapour pressure of a solvent is lowered by dissolving a nonvoltile solute into it. When the solute is nonvolatile it does not contribute to the vapour pressure above the solution. Therefore, the vapour pressure of solution is equal to the vapour pressure of solvent above the solution.

ii. If P_1^0 is the vapour pressure of pure solvent and P_1 is the vapour pressure of solvent above the solution, then

$$P_1 < P_1^0$$

The vapour pressure lowering is

$$\Delta P = P_1^0 - P_1 \quad \text{..... (2.5)}$$

iii. Why the vapour pressure of solution containing nonvolatile solute is lower than that of pure solvent? Vapour pressure of a liquid depends on the ease with which the molecules escape from the surface of liquid. When nonvolatile solute is dissolved in a solvent, some of the surface molecules of solvent are replaced by nonvolatile solute molecules. These solute molecules do not contribute to vapour above the solution. Thus, the number of solvent molecules available for vaporization per unit surface area of solution is less than the number at the surface of pure solvent. As a result the solvent molecules at the surface of solution vaporize at a slower rate than pure solvent. This results in lowering of vapour pressure.

2.7.1 Raoult's law for solutions of nonvolatile solutes : We saw in section 2.5.1 that Raoult's law expresses the quantitative relationship between vapour pressure of solution and vapour pressure of solvent.

In solutions of nonvolatile solutes, the law is applicable only to the volatile solvent. The law states that the vapour pressure of solvent over the solution is equal to the vapour pressure of pure solvent multiplted by its mole fraction in the solution. Thus

$$P_1 = P_1^0 x_1$$

A plot of P_1 versus x_1 is a straight line as shown in Fig. 2.5

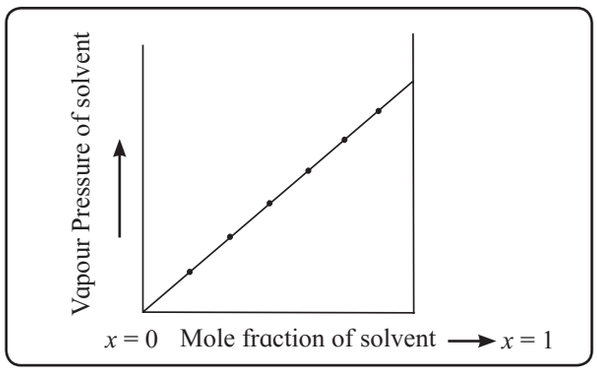


Fig. 2.5 : Variation of vapour pressure of solution with mole fraction of solvent

For a binary solution containing one solute,

$$x_1 = 1 - x_2$$

It therefore, follows that

$$P_1 = P_1^0 x_1$$
$$= P_1^0 (1 - x_2)$$
$$= P_1^0 - P_1^0 x_2$$

or $$P_1^0 - P_1 = P_1^0 x_2$$

The Eq. (2.5) defines $P_1^0 - P_1$ as ΔP, the lowering of vapour pressure. Hence

$$\Delta P = P_1^0 x_2 \quad \text{..... (2.6)}$$

The Eq. (2.6) shows that ΔP depends on x_2 that is on number of solute particles. Thus, ΔP, the lowering of vapour pressure is a colligative property.

2.7.2 Relative lowering of vapour pressure

The ratio of vapour pressure lowering of solvent divided by the vapour pressure of pure solvent is called relative lowering of vapour pressure. Thus

Relative vapour pressure lowering

$$= \frac{\Delta P}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} \quad \text{..... (2.7)}$$

The Eq. (2.6) shows that

$$\frac{\Delta P}{P_1^0} = x_2 = \frac{P_1^0 - P_1}{P_1^0} \quad \text{..... (2.8)}$$

Thus, relative lowering of vapour pressure is equal to the mole fraction of solute in the solution. Therefore, relative vapour pressure lowering is a colligative property.

2.7.3 Molar mass of solute from vapour pressure lowering : We studied that the relative lowering of vapour pressure is equal to the mole fraction x_2 of solute in the solution.

From Eq. 2.6, it follows that :

$$\frac{\Delta P}{P_1^0} = x_2 \quad \text{..... (2.8)}$$

Recall (Chapter 10, sec 10.5.6) that the mole fraction of a component of solution is equal to its moles divided by the total moles in the solution. Thus,

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where n_1 and n_2 are the moles of solvent and solute respectively, in the solution.

We are concerned only with dilute solutions hence $n_1 >> n_2$ and $n_1+n_2 \approx n_1$. The mole fraction x_2 is then given by

$$x_2 = \frac{n_2}{n_1} \quad \text{and}$$

$$\frac{\Delta P}{P_1^0} = \frac{n_2}{n_1} \qquad \ldots\ldots\ldots (2.9)$$

Suppose that we prepare a solution by dissolving W_2 g of a solute in W_1 g of solvent. The moles of solute and solvent in the solution are then,

$$n_2 = \frac{W_2}{M_2} \text{ and } n_1 = \frac{W_1}{M_1} \qquad \ldots\ldots\ldots (2.10)$$

where M_1 and M_2 are molar masses of solvent and solute, respectively. Substitution of Eq. (2.10) into Eq. (2.9) yields

$$x_2 = \frac{\Delta P}{P_1^0} = \frac{W_2/M_2}{W_1/M_1}$$

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1} \qquad \ldots\ldots\ldots (2.11)$$

Knowing all other quantities, molar mass of solute M_2 can be calculated.

Problem 2.4 : A solution is prepared by dissolving 394 g of a nonvolatile solute in 622 g of water. The vapour pressure of solution is found to be 30.74 mm Hg at 30 ^{0}C. If vapour pressure of water at 30 ^{0}C is 31.8 mm Hg, what is the molar mass of solute?

Solution :

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

$W_2 = 394$ g, $W_1 = 622$ g, $M_1 = 18$ g mol^{-1},

$P_1 = 30.74$ mm Hg, $P_1^0 = 31.8$ mm Hg

Substitution of these quantities into the equation gives

$$\frac{31.8 \text{ mm Hg} - 30.74 \text{ mm Hg}}{31.8 \text{ mm Hg}} = \frac{394 \text{ g} \times 18 \text{ gmol}^{-1}}{M_2 \times 622 \text{ g}}$$

$$0.0333 = \frac{11.4 \text{ g mol}^{-1}}{M_2}$$

$$M_2 = \frac{11.4 \text{ g mol}^{-1}}{0.0333} = 342 \text{ g mol}^{-1}$$

Problem 2.5 : The vapour pressure of pure benzene (molar mass 78 g/mol) at a certain temperature is 640 mm Hg. A nonvolatile solute of mass 2.315 g is added to 49 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of solute?

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

$P_1^0 = 640$ mm Hg, $P_1 = 600$ mm Hg,
$W_1 = 49$ g, $W_2 = 2.315$ g

Hence, $\frac{640 \text{ mm Hg} - 600 \text{ mm Hg}}{640 \text{ mm Hg}} = \frac{2.315 \text{ g} \times 78 \text{ g/mol}}{49 \text{ g} \times M_2}$

$$\frac{40 \text{ mm Hg}}{640 \text{ mm Hg}} = \frac{2.315 \text{ g} \times 78 \text{ g/mol}}{49 \text{ g} \times M_2}$$

$$M_2 = \frac{2.315 \text{ g} \times 78 \text{ g/mol} \times 640 \text{ mm Hg}}{40 \text{ mm Hg} \times 49 \text{ g}}$$

$$= 58.96 \text{ g mol}$$

2.8 Boiling point elevation : Recall that the boiling point of liquid is the temperature at which its vapour pressure equals the applied pressure. For liquids in open containers the applied pressure is atmospheric pressure.

It has been found that the boiling point of a solvent is elevated by dissolving a nonvolatile solute into it. Thus, the solutions containing nonvolatile solutes boil at temperatures higher than the boiling point of a pure solvent.

If T_b^0 is the boiling point of a pure solvent and T_b that of a solution, $T_b > T_b^0$. The difference between the boiling point of solution and that of pure solvent at any given constant pressure is called the boiling point elevation.

$$\Delta T_b = T_b - T^0_b \qquad \ldots\ldots\ldots (2.12)$$

2.8.1 Boiling point elevation as a consequence of vapour pressure lowering : To understand the elevation of boiling point, let us compare the vapour pressures of solution and those of pure solvent. The vapour pressures of solution and of pure solvent are plotted as a function of temperature as shown in Fig. 2.6.

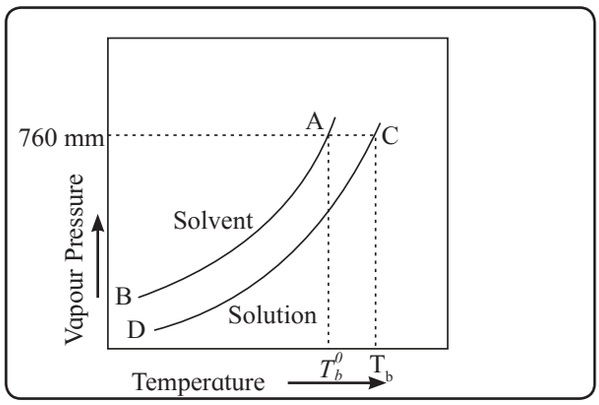


Fig. 2.6 : Vapour pressure-temperature of pure solvent and solution

As stated in section 2.7 that at any temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure-temperature curve of solution (CD) lies below that of solvent (AB). The difference between the two vapour pressures increases as temperature and vapour pressure increase as predicted by the equation

$$\Delta P = x_2 P_1^0$$

The intersection of the curve CD with the line corresponding to 760 mm is the boiling point of solution. The similar intersection of the curve AB is the boiling point of pure solvent. It is clear from the figure that the boiling point (T_b) of the solution is higher than that of pure solvent (T_b^0)

At the boiling point of a liquid, its vapour pressure is equal to 1 atm. In order to reach boiling point, the solution and solvent must be heated to a temperature at which their respective vapour pressures attain 1 atm. At any given temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure of solution needs higher temperature to reach 1 atm than that needed for vapour pressure of solvent. In other words the solution must be heated to higher temperature to cause it to boil than the pure solvent.

2.8.2 Boiling point elevation and concentration of solute : The boiling point elevation is directly proportional to the molality of the solution. Thus,

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m \quad \ldots\ldots\ldots (2.13)$$

where m is the molality of solution. The proportionality constant K_b is called boiling point elevation constant or molal elevation constant or ebullioscopic constant.

If $m = 1$, $\quad \Delta T_b = K_b$

Thus, ebullioscopic constant is the boiling point elevation produced by 1 molal solution.

Units of K_b : $K_b = \dfrac{\Delta T_b}{m} = \dfrac{\text{K}}{\text{mol kg}^{-1}} = \text{K kg mol}^{-1}$

Remember...

K_b and ΔT_b are the differences between two temperatures. Hence, their values will be the same in K or in ^{0}C.

We are dealing with the systems whose temperature is not constant. Therefore, we cannot express the concentration of solution in molarity which changes with temperature whereas molality is temperature independent.

Therefore the concentration of solute is expressed in mol/kg (molality) rather than mol/L (molarity).

2.8.3 Molar mass of solute from boiling point elevation

The Eq. (2.13) is $\Delta T_b = K_b m$

Suppose we prepare a solution by dissolving W_2 g of solute in W_1 g of solvent.

Moles of solute in W_1 g of solvent $= \dfrac{W_2}{M_2}$ where M_2 is the molar mass of solute.

Mass of solvent = W_1 g $= \dfrac{W_1 \text{g}}{1000 \text{ g/kg}} = \dfrac{W_1}{1000}$ kg

Recall the expression of molality, m.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

$$= \frac{W_2/M_2 \text{ mol}}{W_1/1000 \text{ kg}} = \frac{1000\, W_2}{M_2 W_1} \text{ mol kg}^{-1} \quad \ldots\ldots\ldots (2.14)$$

Substitution of this value of m in Eq. (2.13) gives

$$\Delta T_b = K_b \frac{1000\ W_2}{M_2 W_1}$$

Hence,

$$M_2 = \frac{1000\ K_b W_2}{\Delta T_b W_1} \quad \text{..... (2.15)}$$

Problem 2.6 : The normal boiling point of ethyl acetate is 77.06 ^{0}C. A solution of 50 g of a nonvolatile solute in 150 g of ethyl acetate boils at 84.27 ^{0}C. Evaluate the molar mass of solute if K_b for ethyl acetate is 2.77 ^{0}C kg mol^{-1}.

Solution :

$$M_2 = \frac{1000\ K_b W_2}{\Delta T_b W_1}$$

W_2 = 50 g, W_1 = 150 g,

$\Delta T_b = T_b - T^0_b$ = 84.27 ^{0}C - 77.06 ^{0}C

= 7.21^{0}C = 7.21 K

K_b = 2.77 ^{0}C kg mol^{-1} = 2.77 K kg mol^{-1}

Substitution of these in above equation

$$M_2 = \frac{1000 \text{ g Kg}^{-1} \times 2.77 \text{ K kg mol}^{-1} \times 50 \text{ g}}{7.21 \text{ K} \times 150 \text{ g}}$$

= 128 g mol^{-1}

Problem 2.7 : 3.795 g of sulphur is dissolved in 100 g of carbon disulfide. This solution boils at 319.81 K. What is the molecular formula of sulphur in solution? The boiling point of the solvent is 319.45 K.

(Given that K_b for CS_2 = 2.42 K kg mol^{-1} and atomic mass of S = 32 u

$$M_2 = \frac{1000\ K_b W_2}{\Delta T_b W_1}$$

W_1 = 100 g, W_2 = 3.795 g

ΔT_b = (319.81 - 319.45)K = 0.36 K

$$M_2 = \frac{1000 \text{ g kg}^{-1} \times 2.42 \text{ K kg mol}^{-1} \times 3.795 \text{ g}}{0.36 \text{ K} \times 100 \text{ g}}$$

= 255.10 g mol^{-1}

Atomic mass of S = 32 u

Therefore number of atoms in a molecule of sulphur

$$= \frac{\text{molar mass of S}}{\text{atomic mass of S}} = \frac{255.1}{32}$$

= 7.92 ≈ 8

The molecular formula would be S_8 in CS_2

2.9 Depression in freezing point

Recall that freezing point of a liquid is the temperature at which liquid and solid are in equilibrium and the two phases have the same vapour pressure.

The general experimental observation is that the freezing point of a solvent is lowered by dissolving a nonvolatile solute into it. Thus, freezing point of solution containing a nonvolatile solute is lower than that of pure solvent.

If T_f^0 is the freezing point of pure solvent and T_f that of a solution in which nonovolatile solute is dissolved, $T_f^0 > T_f$. The difference between the freezing point of pure solvent and that of the solution is depression in freezing point.

Thus $\Delta T_f = T_f^0 - T_f$ ..... (2.16)

2.9.1 Freezing point depression as a consequence of vapour pressure lowering

The effect of dissolution of a nonvolatile solute into a solvent on freezing point of solvent can be understood in terms of the vapour pressure lowering.

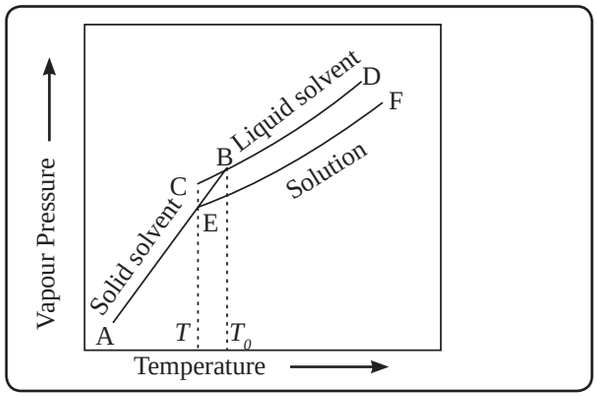


Fig. 2.7 : Variation of vapour pressure with temperature of pure solvent, solid solvent and solution

Consider the vapoure pressure-temperature diagram as shown in Fig. 2.7. The diagram consists of three curves. AB is the vapour pressure curve of solid solvent while CD is the vapour pressure curve of pure liquid solvent. EF is the vapour pressure curve of solution that always lies below the pure solvent.

It is important to note that solute does not dissolve in solid solvent.

The curves AB and CD intersect at point B where solid and liquid phases of pure solvent are in equilibrium. The two phases have the same vapour pressure at B. The temperature corresponding to B is the freezing point of solvent (T_f^0).

Similarly at E, the point of intersection of EF and AB, the solid solvent and solution are in equilibrium. They have the same vapour pressure at E. The temperature corresponding to E is the freezing point of solution, T_f.

It is clear from the figure that freezing point of solution T_f is lower than that of pure solvent T_f^0. It is obvious because the vapour pressure curve of solution lies below that of solvent.

Why freezing point of solvent is lowered by dissolving a nonvolatile solute into it? At the freezing point of a pure liquid the attractive forces among molecules are large enough to cause the change of phase from liquid to solid.

In a solution, the solvent molecules are separated from each other because of solute molecules. Thus, the separation of solvent molecules in solution is more than that in pure solvent. This results in decreasing the attractive forces between solvent molecules. Consequently, the temperature of the solution is lowered below the freezing point of solvent to cause the phase change.

2.9.2 Freezing point depression and concentration of solute : As varified experimentally for a dilute solution the freezing point depression (ΔT_f) is directly proportional to the molality of solution. Thus,

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m \ldots\ldots\ldots (2.17)$$

The proportionality constant K_f is called freezing point depression constant or cryoscopic constant.

If $m = 1$, $\Delta T_f = K_f$. The cryoscopic constant thus is the depression in freezing point produced by 1 molal solution of a nonvolatile solute.

Unit of K_f: $\frac{\Delta T_f}{m} = \frac{\text{K or } ^0\text{C}}{\text{mol kg}^{-1}}$

= K kg mol^{-1} or ^{0}C kg mol^{-1}

2.9.3 Molar mass of solute from freezing point depression

Refer to Eq. (2.17), $\Delta T_f = K_f m$

The molality m of the solution is given by Eq. (2.14) as

$$m = \frac{1000 W_2}{M_2 W_1}$$

Substitution of Eq. (2.14) into Eq. (2.17) gives

$$\Delta T_f = K_f \frac{1000 W_2}{M_2 W_1}$$

Hence, $$M_2 = \frac{1000 K_f W_2}{\Delta T_f W_1} \quad \ldots\ldots\ldots (2.18)$$

Problem 2.8 : 1.02 g of urea when dissolved in 98.5 g of certain solvent decreases its freezing point by 0.211K. 1.609 g of unknown compound when dissolved in 86 g of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the unknown compound.

(Molar mass of urea = 60 g mol^{-1})

Solution :

Urea	Unknown compound
$W_2 = 1.02$ g	$W_2' = 1.609$ g
$W_1 = 98.5$ g	$W_1' = 86$ g
$\Delta T_f = 0.211$ K	$\Delta T_f' = 0.34$ K
$M_2 = 60$ gmol^{-1}	$M_2' = ?$

$$1000 K_f = \frac{M_2 \times \Delta T_f \times W_1}{W_2}$$

$$1000K_f = \frac{M_2' \times \Delta T_f' \times W_1'}{W_2'}$$

$$= \frac{60\ g\ mol^{-1} \times 0.211\ K \times 98.5\ g}{1.02\ g}$$

$$= \frac{M_2' \times 0.34K \times 86\ g}{1.609\ g}$$

$$\frac{1247.01\ g\ K\ mol^{-1}}{1.02} = \frac{M_2' \times 29.24\ K}{1.609}$$

$$1222.55\ g\ K\ mol^{-1} = M_2' \times 18.173$$

$$M_2' = \frac{1222.55\ g\ K\ mol^{-1}}{18.175\ K} = 67.3\ g\ mol^{-1}$$

2.10 Osmotic pressure : Besides the boiling point elevation and freezing point depression, the osmotic pressure is associated with vapour pressure lowering and can be used to determine molar masses of dissolved solutes.

Semipermeable membrane : The osmotic pressure phenomenon involves the use of semipermeable membrane.

It is a film such as cellophane which has pores large enough to allow the solvent molecules to pass through them. These pores are small enough not to allow the passage of large solute molecules or ions of high molecular mass through them. The semi-permeable membrane selectively allows passage of solvent molecules.

2.10.1 Osmosis : When a solution and pure solvent or two solutions of different concentrations are separated by a semi-permeable membrane, the solvent molecules pass through the membrane.

What is the direction of flow of solvent molecules? It is important to understand that the passage of solvent molecules through the semipermeable membrane takes place in both directions, since solvent is on both sides of the membrane. However, the rate of passage of solvent molecules into the solution or from more dilute solution to more concentrated solution is found to be greater than the rate in the reverse direction. This is favourable since the vapour pressure of solvent is greater than that of solution. The net spontaneous flow of solvent molecules into the solution or from more dilute solution to more concentrated solution through a semipermeable membrane is called osmosis. See Fig. 2.8.

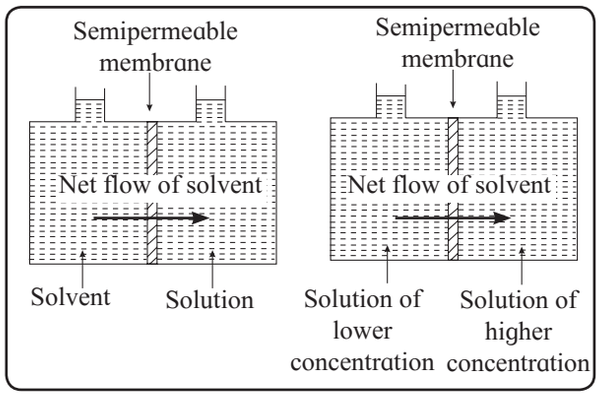


Fig. 2.8 : Osmosis

As a result of osmosis, the amount of liquid on the pure solvent side or more dilute solution side decreases. Consequently, the amount of liquid on the other side increases. This results in decrease of the concentration of solution.

2.10.2 Osmotic pressure : Osmosis can be demonstrated with experimental set up shown in Fig. 2.9

Semipermeable membrane is firmly fastened across the mouth of thistle tube. The solution of interest is placed inside an inverted thistle tube. This part of the tube and the membrane are then immersed in a container of pure water.

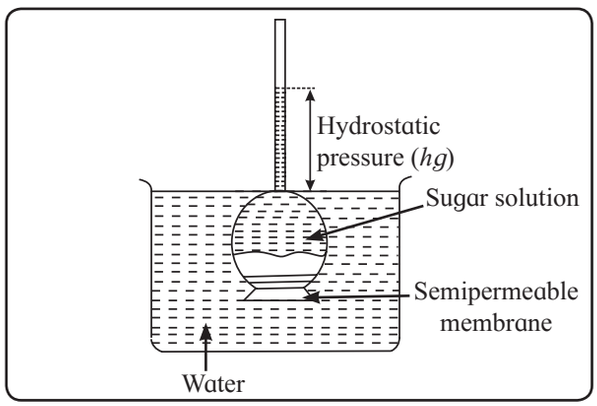


Fig. 2.9 : Osmosis and osmotic pressure

As a result, some of the solvent passes through the membrane into the solution. It causes the liquid level in the tube to rise. The liquid column in the tube creates hydrostatic pressure that pushes the solvent back through the membrane into the container. The column of liquid in the tube continues to rise and eventually stops rising. At this stage hydrostatic pressure developed is sufficient to force solvent molecules back through the membrane into the container at the same rate they enter the solution.

An equilibrium is thus established where rates of forward and reverse passages are equal. The height of liquid column in the tube remains constant. This implies that the hydrostatic pressure has stopped osmosis.

Remember...

It is important to note that osmotic pressure is not the pressure produced by a solution. It exists only when the solution is separated from the solvent by a suitable kind of semipermeable membrane.

The hydrostatic pressure that stops osmosis is an osmotic pressure (π) of the solution. The hydrostatic pressure is equal to $h\rho g$ where h is the height of liquid column in the tube, ρ is density of solution and g is acceleration due to gravity.

2.10.3 Isotonic, hypertonic and hypotonic solutions

i. Isotonic solutions : Two or more solutions having the same osmotic pressure are said to be **isotonic solutions**.

For example, 0.1 M urea solution and 0.1 M sucrose solution are isotonic because their osmotic pressures are equal. Such solutions have the same molar concentrations but different concentrations in g/L. If these solutions are separated by a semipermeable membrane, there is no flow of solvent in either direction.

ii. Hypertonic and hypotonic solutions :

If two solutions have unequal osmotic pressures, the more concentrated solution with higher osmotic pressure is said to be **hypertonic solution**.

The more dilute solution exhibiting lower osmotic pressure is said to be **hypotonic solution**.

For example, if osmotic pressure of sucrose solution is higher than that of urea solution, the sucrose solution is hypertonic to urea solution, and the urea solution is hypotonic to sucrose solution.

2.10.4 Osmotic pressure and concentration of solution

For very dilute solutions, the osmotic pressure follows the equation,

$$\pi = \frac{n_2 RT}{V} \quad \text{.....(2.19)}$$

where V is the volume of a solution in dm^3 containing n_2 moles of nonvolatile solute. R is the gas constant equal to 0.08206 dm^3 atm $K^{-1}mol^{-1}$ and π is osmotic pressure in atm.

The term n_2/V is concentration in molarity (M). Eq. (2.19) thus can be written as

$$\pi = MRT \quad \text{.....(2.20)}$$

Note that the solute concentration is expressed in molarity while calculating osmotic pressure rather than molality. The reason is that osmotic pressure measurements are made at a specific constant temperature. It is not necessary to express concentration in a temperature independent unit like molality.

2.10.5 Molar mass of solute from osmotic pressure

Consider Eq. (2.19) $\pi = \frac{n_2 RT}{V}$

If the mass of solute in V litres of solution is W_2 and its molar mass is M_2 then $n_2 = W_2/M_2$. With this value of n_2, Eq. (2.19) becomes

$$\pi = \frac{W_2 RT}{M_2 V} \text{ or } M_2 = \frac{W_2 RT}{\pi V} \quad \text{.....(2.21)}$$

Remember...

Osmotic pressure is much larger and therefore more precisely measurable property than other colligative properties. It is therefore, useful to determine molar masses of very expensive substances and of the substances that can be prepared in small quantities.

2.10.6 Reverse osmosis : As mentioned earlier osmosis is a flow of solvent through a semipermeable membrane into the solution.

The direction of osmosis can be reversed by applying a pressure larger than the osmotic pressure.

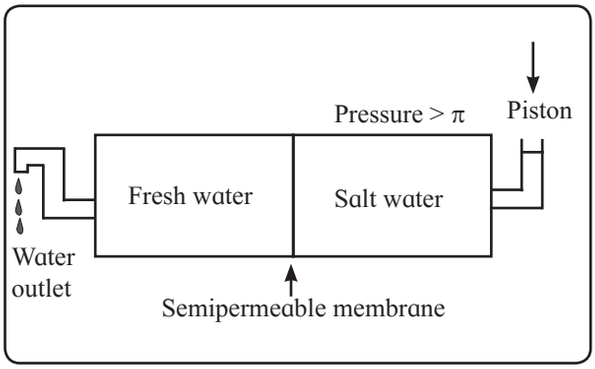


Fig. 2.10 : Reverse osmosis

The pure solvent then flows from solution into pure solvent through semi-permeable membrane. This phenomenon is called reverse osmosis. Fig. 2.10 shows the schematic set up for reverse osmosis. Fresh water and salty water are separated by a semipermeable membrane. When the pressure larger than the osmotic pressure of solution is applied to solution, pure water from salty water passes into fresh pure water through the membrane.

Problem 2.9 : What is the molar mass of a solute if a solution prepared by dissolving 0.822 g of it in 300 mdm^3 of water has an osmotic pressure of 149 mm Hg at 298 K?

Solution :

$$M_2 = \frac{W_2 RT}{\pi V}$$

$W_2 = 0.822$ g

$R = 0.08205$ dm^3 atm K^{-1} mol^{-1}

$T = 298$K

$$\pi = 149 \text{ (mmHg)} = \frac{149 \text{ (mmHg)}}{760 \text{ (mmHg/atm)}}$$

$= 0.196$ atm

$V = 300$ mL $= 0.3$dm^3

$$M_2 = \frac{0.822 \text{ g} \times 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298\text{K}}{0.196 \text{ atm} \times 0.3\text{dm}^3}$$

$= 342$ g mol^{-1}

2.11 Collgative properties of electrolytes

Can you recall ?

Electrolytes and nonelectrolytes.

Solutions of nonelectrolytes in water exhibit colligative properties as described in the preceeding sections. These solutions also give, for the dissolved substances, the molar masses expected from their chemical formulae.

The study of colligative properties of electrolytes, however, require a different approach than used for colligative properties of nonelectrolytes. Following are the experimental observations for the colligative behavior of electrolytes.

i. The solutions of elctrolytes also exhibit colligative properties which do not obey the relations of nonelectrolytes.

ii. The colligative properties of the solutions of electrolytes are greater than those to be expected for solutions of nonelectrolytes of the same concentration.

iii. The molar masses of electrolytes in aqueous solutions determined by colligative properties are found to be considerably lower than the formula masses.

Why the colligative properties of electrolyte solutions are greater than those for nonelectrolyte solutions of the same concentration? Recall that electrolytes dissociate into two or more ions when

dissolved in water whereas nonelctrolytes do not. Stated differently, one formula unit of electrolyte dissolved in water produces two or more ions. Consequently number of particles in solution increases.

The colligative properties of electrolyte solutions are thus higher than the nonelectrolyte solutions.

If 1.25 m sucrose solution has ΔT_f of 2.32°C, what will be the expected value of ΔT_f for 1.25m $CaCl_2$ solution?

For example, when NaCl is dissolved in water, it produces two ions, $Na^{\oplus}$ and $Cl^{\ominus}$, whereas sucrose does not dissociate. It is expected then that the colligative property of 0.1 *m* NaCl is twice that of 0.1 *m* sucrose solution.

2.11.1 van't Hoff factor(i)

To obtain the colligative properties of electrolyte solutions by using relations for nonelectrolytes, van't Hoff suggested a factor *i*. It is defined as the ratio of colligative property of a solution of electrolyte to the collogative property of nonelectrolyte solution of the same concentration. Thus

$$i = \frac{\text{colligative property of electrolyte solution}}{\text{colligative property of nonelectrolyte solution of the same concentration}}$$

$$= \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{(\Delta T_b)}{(\Delta T_b)_0} = \frac{(\Delta P)}{(\Delta P)_0} = \frac{(\pi)}{(\pi)_0} \quad \ldots\ldots\ldots (2.22)$$

where quantities without subscript refer to electrolytes and those with subscript to nonelectrolytes.

The van't Hoff factor *i* is also defined in an alternative but exactly in equivalent manner as

$$i = \frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}} \quad \ldots\ldots\ldots (2.23)$$

$$= \frac{\text{formula mass of substance}}{\text{observed molar mass of substance}}$$

$$= \frac{M_{theoretical}}{M_{observed}} \quad \ldots\ldots\ldots (2.24)$$

Thus, *i* is equal to 1 for nonelctrolyte, 2 for KNO_3 and NaCl, 3 for Na_2SO_4 and $CaCl_2$ and so forth. The colligative properties of these electrolytes are, therefore, twice and thrice respectively as those of noneletrolytes of the same concentration.

The foregoing arguments are valid only for infinitely dilute solutions where the dissociation of electrolytes is complete.

In reality especially at high concentrations, the colligative properties of strong electrolytes and their i values are usually smaller than expected. The reason is that the electrostatic forces between oppositely charged ions bring about the formation of ion pairs. Each ion pair consists of one or more cations and one or more anions held together by electrostatic attractive forces. This results in decrease in the number of particles in solution causing reduction in the expected i value and colligative properties.

2.11.2 Modification of expressions of colligative properties : The expressions of colligative properties mentioned earlier for nonelectrolytes are to be modified so as to make them applicable for electrolyte solutions. The modified equations are

i. $\Delta P = i\ P_1^0 x_2 = i\frac{W_2 M_1}{M_2 W_1} \times P_1^0$

ii. $\Delta T_b = iK_b m = i\frac{1000\ K_b W_2}{M_2 W_1}$

iii. $\Delta T_f = i\ K_f m = i\ \frac{1000\ K_f W_2}{M_2 W_1}$

iv. $\pi = i\ MRT = i\frac{W_2 RT}{M_2 V}$

2.11.3 van't Hoff factor and degree of dissociation : A discussion of colligative properties of electrolytes in the preceeding sections is based on the fact that the elctrolytes are completely dissociated in their aqueous solutions. This is approximately true

for solutions of strong electrolytes and not for weak electrolytes that dissociate to a small extent. The weak electrolytes involve the concept of degree of dissociation (∝), that changes the van't Hoff factor.

Relation between van't Hoff factor and degree of dissociation

Consider an elctrolyte A_xB_y that dissociates in aqueous solution as

$$AxBy \rightleftharpoons x\ A^{y\oplus} + y\ B^{z\ominus} \quad .....(2.25)$$

Initially : 1 mol 0 0

At equilibrium :

(1-∝) mol (x ∝ mol) (y ∝) mol

If ∝ is the degree of dissociation of elctrolyte, then the moles of cations are ∝x and those of anions are ∝y at equilibrium. We have dissolved just 1 mol of electrolyte initially. ∝ mol of eletrolyte dissociates and (1-∝) mol remains undissociated at equilibrium.

Total moles after dissociation

$$= (1- \propto) + (x\propto) + (y\propto)$$

$$= 1+\propto(x+y-1)$$

$$= 1+\propto(n-1) \ldots\ldots\ldots (2.26)$$

where, n = x+y = moles of ions obtained from dissociation of 1 mole of electrolyte.

The van't Hoff factor given by Eq. (2.23) is

$$i = \frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}}$$

$$= \frac{1 + \propto(n-1)}{1}$$

Hence $i = 1 + \propto(n-1)$ or $\propto = \frac{i - 1}{n - 1}$ .....(2.27)

Problem 2.10 : 0.2 *m* aqueous solution of KCl freezes at -0.680 ^{0}C. Calculate van't Hoff factor and osmotic pressure of solution at 0 ^{0}C.(K_f = 1.86 K kg mol^{-1})

Solution :

$$\Delta T_f = K_f m$$

ΔT_f = 0.680 K, m = 0.2 mol kg^{-1}

$(\Delta T_f)_0$ = 1.86 K kg mol^{-1} × 0.2 mol kg^{-1}

= 0.372 K

$$i = \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{0.680\ K}{0.372\ K} = 1.83$$

$$(\pi)_0 = MRT$$

$$= \frac{n_2}{V}RT$$

$$= \frac{0.2\ mol \times 0.08205\ L\ atm.mol^{-1}K^{-1} \times 273K}{1L}$$

= 4.48 atm

$$i = 1.83 = \frac{\pi}{\pi_0}$$

$$\pi = 1.83 \times 4.48\ atm$$

$$\pi = 8.2\ atm$$

Problem 2.11 : 0.01*m* aqueous formic acid solution freezes at -0.021 ^{0}C. Calculate its degree of dissociation. K_f = 1.86 K kg mol^{-1}

$\Delta T_f = i\ K_f m$

ΔT_f = 0 ^{0}C - (-0.021 ^{0}C) = 0.021 ^{0}C

m = 0.01 mol kg^{-1}

0.021 = i × 1.86 K kg mol^{-1} ×0.01 mol kg^{-1}

$$i = \frac{0.021}{1.86 \times 0.01} = 1.13$$

$$\propto = \frac{i - 1}{n - 1} = i - 1 \text{ because } n = 2$$

Hence, ∝ = 1.13 - 1 = 0.13 = 13%

Problem 2.12 : 3.4 g of $CaCl_2$ is dissolved in 2.5 L of water at 300 K. What is the osmotic pressure of the solution? van't Hoff factor for $CaCl_2$ is 2.47.

Solution :

$$\pi = iMRT = i\frac{W_2RT}{M_2V}$$

i = 2.47, W_2 = 3.4 g, R = 0.08206 dm^{3}atm K^{-1} mol^{-1}, T = 300 K, M_2 = 40+71 = 111 g mol^{-1}, V = 2.5 dm^3

$$\pi = 2.47 \times \frac{3.4\ \cancel{g} \times 0.08206\ \cancel{dm^3}\ atm\ \cancel{K^{-1}}\ \cancel{mol^{-1}} \times 300\ \cancel{K}}{111\ \cancel{g\ mol^{-1}} \times 2.5\ \cancel{dm^3}}$$

= 0.745 atm

Problem 2.13 : Which of following solutions will have maximum boiling point elevation and which have minimum freezing point depression assuming the complete dissociation? (a) 0.1 *m* KCl (b) 0.05 *m* NaCl (c) 1*m* $AlPO_4$ (d) 0.1 *m* $MgSO_4$

Solution : Boiling point elevation and freezing point depression are colligative properties that depend on number of particles in solution. The solution having more number of particles will have large boiling point elevation and that having less number of particles would show minimum freezing point depression.

(a) $KCl \longrightarrow K^{\oplus} + Cl^{\ominus}$ Total particles in
0.1m 0.1m 0.1m solution = 0.2 mol

(b) $NaCl \longrightarrow Na^{\oplus} + Cl^{\ominus}$ Total particles in
0.05m 0.05m 0.05m solution = 0.1 mol

(c) $AlPO_4 \longrightarrow Al^{3\oplus} + PO_4^{3\ominus}$ Total particles in
1m 1m 1m solution = 2.0mol

(d) $MgSO_4 \longrightarrow Mg^{2\oplus} + SO_4^{2\ominus}$ Total particles in
0.1m 0.1m 0.1m solution = 0.2mole

$AlPO_4$ solution contains highest moles and hence highest number particles and in turn, the maximum ΔT_b. NaCl solution has minimum moles and particles. It has minimum ΔT_f.

Arrange the following solutions in order of increasing osmotic pressure. Assume complete ionization. a) 0.5m Li_2SO_4 b) 0.5m KCl c) 0.5m $Al_2(SO_4)_3$ d) 0.1m $BaCl_2$.

Problem 2.14 : Assuming complete dissociation, calculate the molality of an aqueous solution of KBr whose freezing point is -2.95^{0}C. K_f for water is 1.86 K kg mol^{-1}

Solution :

$KBr = K^{\oplus} + Br^{\ominus}$,

$i = \dfrac{\text{moles of particles after dissociation}}{\text{moles of particles dissolved}}$

$= \dfrac{2}{1} = 2$

$\Delta T_f = iK_f m$

$\Delta T_f = 0\ ^0C - (-2.95\ ^0C) = 2.95\ ^0C$

$$m = \frac{\Delta T_f}{iK_f} = \frac{2.95\ K}{2 \times 1.86\ K\ kg\ mol^{-1}}$$

$= 0.793\ mol\ kg^{-1}$

Exercises

1. Choose the most correct option.

i. The vapour pressure of a solution containing 2 moles of a solute in 2 moles of water (vapour pressure of pure water = 24 mm Hg) is
a. 24 mm Hg b. 32 mm Hg
c. 48 mm Hg d. 12 mm Hg

ii. The colligative property of a solution is
a. vapour pressure b. boiling point
c. osmotic pressure d. freezing point

iii. In calculating osmotic pressure the concentration of solute is expressed in
a. molarity b. molality
c. mole fraction d. mass percent

iv. Ebullioscopic constant is the boiling point elevation when the concentration of solution is
a. 1m b. 1M c. 1 mass%
d. 1 mole fraction of solute.

v. Cryoscopic constant depends on
a. nature of solvent
b. nature of solute
c. nature of solution
d. number of solvent molecules

vi. Identify the correct statement

a. vapour pressure of solution is higher than that of pure solvent.
b. boiling point of solvent is lower than that of solution
c. osmotic pressure of solution is lower than that of solvent
d. osmosis is a colligative property.

vii. A living cell contains a solution which is isotonic with 0.3 M sugar solution. What osmotic pressure develops when the cell is placed in 0.1 M KCl solution at body temperature?

a. 5.08 atm b. 2.54 atm
c. 4.92 atm d. 2.46 atm

viii. The osmotic pressure of blood is 7.65 atm at 310 K. An aqueous solution of glucose isotonic with blood has the percentage (by volume)

a. 5.41 % b. 3.54 %
c. 4.53 % d. 53.4 %

ix. Vapour pressure of a solution is

a. directly proportional to the mole fraction of the solute
b. inversely proportional to the mole fraction of the solute
c. inversely proportional to the mole fraction of the solvent
d. directly proportional to the mole fraction of the solvent

x. Pressure cooker reduces cooking time for food because

a. boiling point of water involved in cooking is increased
b. heat is more evenly distributed in the cooking space
c. the higher pressure inside the cooker crushes the food material
d. cooking involves chemical changes helped by a rise in temperature.

xi. Henry's law constant for a gas CH_3Br is 0.159 $moldm^{-3}$ atm at 25 ^0C. What is the solubility of CH_3Br in water at 25 ^0C and a partial pressure of 0.164 atm?

a. 0.0159 mol L^{-1} b. 0.164 mol L^{-1}
c. 0.026 M d. 0.042 M

xii. Which of the following statement is NOT correct for 0.1 M urea solution and 0.05 M sucrose solution?

a. osmotic pressure exhibited by urea solution is higher than that exhibited by sucrose solution
b. urea solution is hypertonic to sucrose solution
c. they are isotonic solutions
d. sucrose solution is hypotonic to urea solution

2. Answer the following in one or two sentences

i. What is osmotic pressure?

ii. A solution concentration is expressed in molarity and not in molality while considering osmotic pressure. Why?

iii. Write the equation relating boiling point elevation to the concentration of solution.

iv. A 0.1 m solution of K_2SO_4 in water has freezing point of -4.3 ^0C. What is the value of van't Hoff factor if K_f for water is 1.86 K kg mol^{-1}?

v. What is van't Hoff factor?

vi. How is van't Hoff factor related to degree of ionization?

vii. Which of the following solutions will have higher freezing point depression and why ?

a. 0.1 *m* NaCl b. 0.05 *m* $Al_2(SO_4)_3$

viii. State Raoult's law for a solution containing a nonvolatile solute

ix. What is the effect on the boiling point of water if 1 mole of methyl alcohol is added to 1 dm^3 of water? Why?

x. Which of the four colligative properties is most often used for molecular mass determination? Why?

3. Answer the following.

i. How vapour pressure lowering is related to a rise in boiling point of solution?

ii. What are isotonic and hypertonic solutions?

iii. A solvent and its solution containing a nonvolatile solute are separated by a semipermable membrane. Does the flow of solvent occur in both directions? Comment giving reason.

iv. The osmotic pressure of $CaCl_2$ and urea solutions of the same concentration at the same temperature are respectively 0.605 atm and 0.245 atm. Calculate van't Hoff factor for $CaCl_2$

v. Explain reverse osmosis.

vi. How molar mass of a solute is determined by osmotic pressure measurement?

vii. Why vapour pressure of a solvent is lowered by dissolving a nonvolatile solute into it?

viii. Using Raoult's law, how will you show that $\Delta P = P_1^0 x_2$? Where x_2 is the mole fraction of solute in the solution and P_1^0 vapour pressure of pure solvent.

ix. While considering boiling point elevation and freezing point depression a solution concentration is expressed in molality and not in molarity. Why?

4. Derive the relationship between degree of dissociation of an electrolyte and van't Hoff factor.

5. What is effect of temperature on solubility of solids in water? Give examples.

6. Obtain the relationship between freezing point depression of a solution containing nonvolatile nonelctrolyte and its molar mass.

7. Explain with diagram the boiling point elevation in terms of vapour pressure lowering.

8. Fish generally needs O_2 concentration in water at least 3.8 mg/L for survival. What partial pressure of O_2 above the water is needed for the survival of fish? Given the solubility of O_2 in water at 0^0C and 1 atm partial pressure is 2.2×10^{-3} mol/L (0.054 atm)

9. The vapour pressure of water at 20 ^{0}C is 17 mm Hg. What is the vapour pressure of solution containing 2.8 g urea in 50 g of water? (16.17 mm Hg)

10. A 5% aqueous solution (by mass) of cane sugar (molar mass 342 g/mol) has freezing point of 271K. Calculate the freezing point of 5% aqueous glucose solution. (269.06 K)

11. A solution of citric acid $C_6H_8O_7$ in 50 g of acetic acid has a boiling point elevation of 1.76 K. If K_b for acetic acid is 3.07 K kg mol^{-1}, what is the molality of solution? (0.573 m)

12. An aqueous solution of a certain organic compound has a density of 1.063 gmL^{-1}, an osmotic pressure of 12.16 atm at 25^{0}C and a freezing point of -1.03^{0}C. What is the molar mass of the compound? (334 g/mol)

13. A mixture of benzene and toluene contains 30% by mass of toluene. At 30^{0}C, vapour pressure of pure toluene is 36.7 mm Hg and that of pure benzene is 118.2 mm Hg. Assuming that the two liquids form ideal solutions, calculate the total pressure and partial pressure of each constituent above the solution at 30^{0}C. (86.7 mm, P = 96.5 mm)

14. At 25 ^{0}C a 0.1 molal solution of CH_3COOH is 1.35 % dissociated in an aqueous solution. Calculate freezing point and osmotic pressure of the solution assuming molality and molarity to be identical. (-0.189 ^{0}C, 2.48 atm)

15. A 0.15 m aqueous solution of KCl freezes at -0.510 ^{0}C. Calculate *i* and osmotic pressure at 0 ^{0}C. Assume volume of solution equal to that of water (1.83, 6.15 atm)

Activity :

Boil about 100 mL of water in a beaker. Add about 10 to 15 g of salt (NaCl) to the boiling water. Write your observations and conclusions.

3. IONIC EQUILIBRIA

Can you recall ?

- What is chemical equilibrium ?
- What are electrolytes ?

3.1 Introduction : The equilibrium between ions and unionized molecules in solution is called ionic equilibrium. The principles of chemical equilibrium we studied in standard XI will be applied to ionic equilibria. In this chapter with the help of these principles we determine equilibrium constants and concentrations of ions and unionized species. In particular examine the following ionic equilibria :

- $H^{\oplus}$ and $OH^{\ominus}$ ions and unionized water molecules.
- Ionization of weak acids and weak bases.
- Reactions between ions of salt and ions of water.
- Solid salt and its ions in water.

3.2 Types of electrolyte : The substances which give rise to ions when dissolved in water are electrolytes. The non electrolytes are those which do not ionize and exist as molecules in aqueous solutions.

The electrolytes are classified into strong and weak electrolytes. This classification is based on their extent of ionisation in dilute aqueous solutions.

3.2.1 Strong electrolyte : The electrolytes ionizing completely or almost completely are strong electrolytes. For example : strong acids, strong bases and salts.

3.2.2 Weak electrolyte : The electrolytes which dissociate to a smaller extent in aqueous solution are weak electrolytes. Weak acids and weak bases belong to this class.

The weak electrolytes dissociate only partially in dilute aqueous solutions. An equilibrium thus can be established between the ions and nonionized molecules. The ionization reaction therein is represented as double arrow($\rightleftharpoons$) between the ions and nonionized molecule.

Use your brain power

Which of the following is a strong electrolyte ?

HF, AgCl, $CuSO_4$, CH_3COONH_4, H_3PO_4.

3.2.3 Degree of dissociation ($\propto$) : The degree of dissociation of an electrolyte is defined as a fraction of total number of moles of the electrolyte that dissociates into its ions when the equilibrium is attained. It is denoted by symbol $\propto$ and given by

$$\propto = \frac{\text{number of moles dissociated}}{\text{total number of moles}} \quad \ldots\ldots (3.1)$$

$$\text{Percent dissociation} = \propto \times 100 \quad \ldots\ldots (3.2)$$

If 'c' is the molar concentration of an electrolyte the equilibrium concentration of cation or anion is ($\propto \times c$) mol dm^{-3}.

3.3 Acids and Bases : Acids and bases are familiar chemical compounds. Acetic acid is found in vinegar, citric acid in lemons, magnesium hydroxide in antacids, ammonia in household cleaning products. The tartaric acid is present in tamarind paste. These are some acids and bases we come across in everyday life.

3.3.1 Arrhenius theory of acids and bases

According to this theory acids and bases are defined as follows :

Acid : Acid is a substance which contains hydrogen and gives rise to $H^{\oplus}$ ions in aqueous solution. For example :

$$HCl\ (aq) \xrightarrow{water} H^{\oplus}(aq) + Cl^{\ominus}(aq)$$

$$CH_3COOH(aq) \underset{}{\overset{water}{\rightleftharpoons}} CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

Arrhenius described $H^{\oplus}$ ions in water as bare ions; they hydrate in aqueous solutions and thus represented as hydronium ions $H_3O^{\oplus}$. We herewith conveniently represent them as $H^{\oplus}$.

Do you know ?

Hydrochloric acid, HCl present in the gastric juice is secreted by our stomach and is essential for digestion of food.

Base : Base is a substance that contains OH group and produces hydroxide ions ($OH^{\ominus}$) ions in aqueous solution. For example,

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Arrhenius theory accounts for properties of different acids and bases and is applicable only to aqueous solutions. It does not account for the basicity of NH_3 and Na_2CO_3 which do not have OH group.

3.3.2 Bronsted - Lowry theory :

J. N. Bronsted and T. M. Lowry (1923) proposed a more general theory known as the Bronsted-Lowry proton transfer theory. According to this theory acids and bases are defined as follows.

Acid : Acid is a substance that donates a proton ($H^{\oplus}$) to another substance.

Base : Base is a substance that accepts a proton ($H^{\oplus}$) from another substance.

For example :

$$\underset{Acid_1}{HCl} + \underset{Base_2}{NH_3} \rightleftharpoons \underset{Acid_2}{NH_4^{\oplus}} + \underset{Base_1}{Cl^{\ominus}}$$

In the above reaction HCl and $NH_4^{\oplus}$ are proton donors and act as acids. The NH_3 and $Cl^{\ominus}$ are proton acceptors and act as bases. Further it follows that the products of the Bronsted-Lowry acid-base reactions are acids bases.

The base produced by releasing the proton from an acid is the conjugate base of that acid. Likewise the acid produced when a base accepts a proton is called the conjugate acid of that base. A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair**.

$$\underset{Acid_1}{HCl(aq)} + \underset{Base_2}{H_2O(l)} \rightleftharpoons \underset{Acid_2}{H_3O^{\oplus}(aq)} + \underset{Base_1}{Cl^{\ominus}(aq)}$$

conjugate acid-base pair$_2$

conjugate acid-base pair$_1$

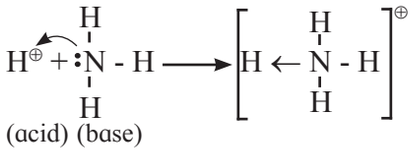
3.3.3 Lewis theory :

A more generalized acid-base concept was put forward by G.N. Lewis in 1923. According to this theory acids and bases are defined as follows.

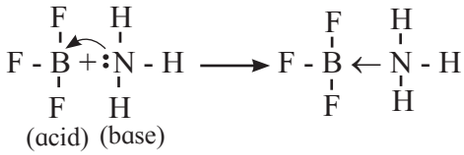
Acid : Any species that accepts a share in an electron pair is called Lewis acid.

Base : Any species that donates a share in an electron pair is called Lewis base.

For example :



(acid) (base)



(acid) (base)

Use your brain power

- All Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids. Explain.

Amphoteric nature of water : Water has the ability to act as an acid as well as a base. Such behaviour is known as amphoteric nature of water. For example :

$H_2O(l) + NH_3(aq) \rightleftharpoons OH^{\ominus}(aq) + NH_4^{\oplus}(aq)$

Acid

$H_2O(l) + HCl(aq) \rightleftharpoons H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$

Base

H_2O acts as an acid towards NH_3 and as a base towards HCl. Therefore H_2O is amphoteric.

3.4 Ionisation of acids and bases

Acids and bases are classified as strong acids and strong bases, weak acids and weak bases on the basis of their **extent of dissociation**. Strong acids and bases are almost completely dissociated in water. For example :

$HCl\ (aq) \longrightarrow H^{\oplus}(aq) + Cl^{\ominus}\ (aq)$

$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$

Typical strong acids are HCl, HNO_3, H_2SO_4, HBr and HI while typical strong bases may include NaOH and KOH.

Weak acids and weak bases are partially dissociated in water. The solution of a weak acid or a weak base contains undissociated molecules along with a small number of ions at equilibrium. For example :

$CH_3COOH(aq) \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$

$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$

Note that HCOOH, HF, H_2S are examples of weak acids while $Fe(OH)_3$, $Cu(OH)_2$ are examples of weak bases.

3.4.1 Dissociation constant of weak acids and weak bases : The dissociation of a weak acid HA in water is expressed as

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$

The equilibrium constant called acid-dissociation constant for this equilibrium is :

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \qquad \ldots\ldots\ldots\ldots (3.3)$$

Similarly the dissociation of weak base BOH in water is represented as :

$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$

The equilibrium constant called base-dissociation constant for this equilibrium is,

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]} \qquad \ldots\ldots\ldots\ldots (3.4)$$

Thus, the dissociation constant of a weak acid or a weak base is defined as **the equilibrium constant for dissociation equilibrium of weak acid or weak base, respectively**.

3.4.2 Ostwald's dilution law : Arrhenius concept of acids and bases was expressed quantitatively by F. W. Ostwald in the form of the dilution law in 1888.

a. Weak acids : Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly $H^{\oplus}$ and $A^{\ominus}$ ions. Then

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$

The acid dissociation constant is given by Eq. (3.3)

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium the fraction dissociated would be $\propto$, where $\propto$ is degree of dissociation of the acid. The fraction of an acid that remains undissociated would be $(1 - \propto)$.

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$			
Amount present at equilibrium/ mol	$(1-\alpha)$	α	α
concentration at equilibrium/ mol dm^{-3}	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

Thus, at equilibrium $[HA] = \frac{1-\alpha}{V}$, mol dm^{-3},

$[H^{\oplus}] = [A^{\ominus}] = \frac{\alpha}{V}$ mol dm^{-3}.

Substituting these in Eq. (3.3)

$$K_a = \frac{(\alpha/V)(\alpha/V)}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V} \quad \ldots\ldots (3.5)$$

If c is the initial concentration of an acid in mol dm^{-3} and V is the volume in $dm^3\ mol^{-1}$ then $c = 1/V$. Replacing $1/V$ in Eq. (3.5) by c we get

$$K_a = \frac{\alpha^2 c}{1-\alpha} \quad \ldots\ldots (3.6)$$

For the weak acid HA, α is very small, or $(1 - \alpha) \cong 1$. With this Eq. (3.5) and (3.6) reduce.

$$K_a = \alpha^2/V \text{ and } K_a = \alpha^2 c \quad \ldots\ldots (3.7)$$

$$\alpha = \sqrt{\frac{K_a}{c}} \text{ or } \alpha = \sqrt{K_a . V} \quad \ldots\ldots (3.8)$$

The Eq. (3.8) implies that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration or directly proportional to the square root of volume of the solution containing 1 mol of the weak acid.

b. Weak base : Consider 1 mol of weak base BOH dissolved in V dm^3 of solution. The base dissociates partially as

$$BOH\ (aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

The base dissociation constant is

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$$

Let the fraction dissociated at equilibrium is α and that remains undissociated is $(1 - \alpha)$.

$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$			
Amount present at equilibrium	$(1-\alpha)$	α	α
concentration at equilibrium	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

A equilibrium,

$[BOH] = \frac{1-\alpha}{V}$ mol dm^{-3},

$[B^{\oplus}] = [OH^{\ominus}] = \frac{\alpha}{V}$ mol dm^{-3}.

Substitution of these concentrations in Eq. (3.4), gives

$$K_b = \frac{(\alpha/V)(\alpha/V)}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V} \quad \ldots\ldots (3.9)$$

Similar arguments in the case of weak acid, led to

$$K_b = \frac{\alpha^2 c}{(1-\alpha)} \quad \ldots\ldots (3.10)$$

$$\alpha = \sqrt{K_b . V}\ , \ \alpha = \sqrt{\frac{K_b}{c}} \quad \ldots\ldots (3.11)$$

The degree of dissociation of a weak base is inversely proportional to square root of its concentration and is directly proportional to square root of volume of the solution containing 1 mol of weak base.

Problem 3.1 : A weak monobasic acid is 0.05% dissociated in 0.02 M solution. Calculate dissociation constant of the acid.

Solution : The dissociation constant of acid is given by $K_a = \alpha^2 c$. Here,

$$\alpha = \frac{\text{percent dissociation}}{100} = \frac{0.05}{100} = 5 \times 10^{-4}$$

$c = 0.02\ M = 2 \times 10^{-2}\ M$

Hence $K_a = (5 \times 10^{-4})^2 \times 2 \times 10^{-2}$

$= 25 \times 10^{-8} \times 2 \times 10^{-2}$

$= 50 \times 10^{-10} = 5 \times 10^{-9}$

Problem 3.2 : The dissociation constant of NH_4OH is 1.8×10^{-5}. Calculate its degree of dissociation in 0.01 M solution.

Solution : The degree of dissociation is given by $\alpha = \sqrt{K_b/c}$. Here,

$K_b = 1.8 \times 10^{-5}$; $c = 0.01 = 1 \times 10^{-2}$ M

Hence, $\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}}$

$= \sqrt{18 \times 10^{-4}} = 4.242 \times 10^{-2} = 0.04242$

Problem 3.3 : A weak monobasic acid is 12% dissociated in 0.05 M solution. What is percent dissociation in 0.15 M solution.

Solution : If α_1 and α_2 are the values of degree of dissociation at two different concentrations c_1 and c_2 respectively, then

$K_a = \alpha_1^2 c_1 = \alpha_2^2 c_2$ Therefore $\alpha_1^2 c_1 = \alpha_2^2 c_2$

$\alpha_1 = \frac{12}{100}$ $c_1 = 0.05$ M, $c_2 = 0.15$ M,

$\alpha_2 = ?$

Substituting these values in the equation gives

$(0.12)^2 \times 0.05 = \alpha_2^2 \times 0.15$

$\alpha_2^2 = \frac{(12)^2 \times 0.05}{0.15} = 0.0048$

Hence $\alpha_2 = 0.0693$ %

$\therefore$ percent dissociation = 6.93 %

Problem 3.4 : Calculate $[H_3O^{\oplus}]$ in 0.1 mol dm^3 solution of acetic acid.

Given : $K_a\,[CH_3COOH] = 1.8 \times 10^{-5}$

Solution : Let α_1 be the degree of dissociation. Concentrations of various species involved at equilibrium are as follows.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^{\ominus} + H_3O^{\oplus}$$
$$(1-\alpha)c \qquad \alpha c \qquad \alpha c$$

$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}}$

$= 1.34 \times 10^{-2}$

$[H_3O^{\oplus}] = \alpha \times c = 1.34 \times 10^{-2} \times 0.1$

$= 1.34 \times 10^{-3}$ mol/L

3.5 Autoionization of water : Pure water ionizes to a very small extent. The ionization equilibrium of water is represented as,

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

The equilibrium constant (K) for the ionization of water is given by

$$K = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{[H_2O]^2} \qquad \ldots\ldots\ldots\ldots (3.12)$$

or $K[H_2O]^2 = [H_3O^{\oplus}][OH^{\ominus}]$ ..... (3.13)

A majority of H_2O molecules are undissociated, consequently concentration of water $[H_2O]$ can be treated as constant. Then

$[H_2O]^2 = K'$. Substituting this in Eq. (3.13) we get,

$$K \times K' = [H_3O^{\oplus}][OH^{\ominus}] \qquad \ldots\ldots\ldots\ldots (3.14)$$

$$K_w = [H_3O^{\oplus}][OH^{\ominus}]$$

where $K_w = KK'$ is called ionic product of water. The product of molar concentrations of hydronium (or hydrogen) ions and hydroxyl ions at equilibrium in pure water at the given temperature is called ionic product of water.

In pure water $H_3O^{\oplus}$ ion concentration always equals the concentration of $OH^{\ominus}$ ion. Thus at 298 K this concentration is found to be 1.0×10^{-7} mol/L.

$K_w = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$

$K_w = 1.0 \times 10^{-14}$ ..... (3.15)

Internet my friend

Find out the values of ionic product K_w of water at various temperatures.

273 K, 283K, 293K, 303K, 313K, 323 K

3.6 pH Scale : Instead of writing concentration of $H_3O^{\oplus}$ ions in mol dm^{-3}, sometimes it is convenient to express it on the logarithmic scale. This is known as pH scale.

Sorensen in 1909 defined the pH of a solution as the negative logarithm to the base 10, of the concentration of $H^{\oplus}$ ions in solution in mol dm^{-3}. Expressed mathematically as

$pH = -\log_{10}[H^{\oplus}]$

Similarly *pOH* of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of $OH^{\ominus}$ ions in solution.

Thus, $pOH = -\log_{10}[OH^{\ominus}]$ ..... (3.16)

3.6.1 Relationship between pH and pOH

The ionic product of water is

$K_w = [H_3O^{\oplus}][OH^{\ominus}]$

Now, $K_w = 1 \times 10^{-14}$ at 298 K and thus

$[H_3O^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}$

Taking logarithm of both the sides, we write

$\log_{10}[H_3O^{\oplus}] + \log_{10}[OH^{\ominus}] = -14$

$-\log_{10}[H_3O^{\oplus}] + \{-\log_{10}[OH^{\ominus}]\} = 14$

From Eq. (3.16) and (3.17)

$pH + pOH = 14$ ..... (3.18)

3.6.2 Acidity, basicity and neutrality of aqueous solutions

1. Neutral solution : For pure water or any aqueous neutral solution at 298 K

$[H_3O^{\oplus}] = [OH^{\ominus}] = 1.0 \times 10^{-7}$ M

Hence, $pH = -\log_{10}[H^{\oplus}] = -\log_{10}[1 \times 10^{-7}] = 7$

2. Acidic solution : In acidic solution, there is excess of $H_3O^{\oplus}$ ions, or $[H_3O^{\oplus}] > [OH^{\ominus}]$ Hence, $[H_3O^{\oplus}] > 1 \times 10^{-7}$ and $pH < 7$

3. Basic solution : In basic solution, the excess of $OH^{\ominus}$ ions are present that is $[H_3O^{\oplus}] < [OH^{\ominus}]$ or $[H_3O^{\oplus}] < 1.0 \times 10^{-7}$ with $pH > 7$.

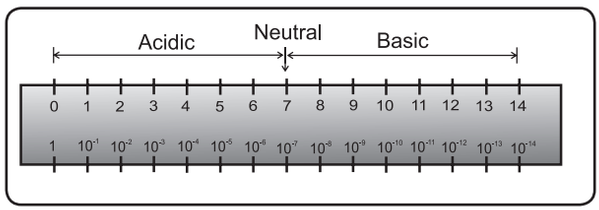


Fig. 3.1 : *pH* scale

Problem 3.5 : Calculate *pH* and *pOH* of 0.01 M HCl solution.

Solution : HCl is a strong acid. It dissociates almost completely in water as

$HCl\ (aq) + H_2O(l) \longrightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$

Hence, $[H_3O^{\oplus}] = c = 0.01M = 1 \times 10^{-2}$ M

$pH = -\log_{10}[H_3O^{+}] = -\log_{10}[1 \times 10^{-2}] = 2$

We know that $pH + pOH = 14$

$\therefore pOH = 14 - pH = 14 - 2 = 12$

Problem 3.6 : *pH* of a solution is 3.12. Calculate the concentration of $H_3O^{\oplus}$ ion.

Solution : *pH* is given by

$pH = -\log_{10}[H_3O^{\oplus}]$

$\log_{10}[H_3O^{\oplus}] = -pH$

$= -3.12$

$= -3 - 0.12 + 1 - 1$

$= (-3 - 1) + 1 - 0.12$

$= -4 + 0.88 = \bar{4}.88$

Thus $[H_3O^{\oplus}] = \text{antilog}\ [\bar{4}.88]$

$= 7.586 \times 10^{-4}$ M

Problem 3.7 : A weak monobasic acid is 0.04 % dissociated in 0.025M solution. What is *pH* of the solution ?

Solution : A weak monobasic acid HA dissociates as :

$HA + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + A^{\ominus}(aq)$

Percent dissociation $= \alpha \times 100$

or $\alpha = \dfrac{\text{percent dissociation}}{100}$

$= \dfrac{0.04}{100} = 4 \times 10^{-4}$

Now $[H_3O^{\oplus}] = \alpha \times c$

$= 4 \times 10^{-4} \times 0.025$ M $= 10^{-5}$ M

$\therefore pH = -\log_{10}[H_3O^{\oplus}] = -\log_{10}[10^{-5}] = 5$

Use your brain power

- Suppose that *pH* of monobasic and dibasic acid is the same. Does this mean that the molar concentrations of both acids are identical ?
- How *pH* of pure water vary with temperature ? Explain.

Problem 3.8 : The *pH* of monoacidic weak base is 11.2. Calculate its percent dissociation in 0.02 M solution.

Solution : *pOH* of the solution is given as :

$$pOH = 14 - pH = 14 - 11.2 = 2.8$$

$$pOH = -\log_{10}[OH^{\ominus}]$$

$$\log_{10}[OH^{\ominus}] = -\,pOH$$

$$= -\,2.8 = -\,2 - 0.8 - 1 + 1$$

$$= -\,3 + 0.2 = \bar{3}.2$$

$$[OH^{\ominus}] = \text{antilog } \bar{3}.2 = 1.585 \times 10^{-3} \text{ mol/dm}^3$$

For monoacidic base,

$$BOH\ (aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$[OH^{\ominus}] = \propto c$$

$$\propto = \frac{[OH^{\ominus}]}{c} = \frac{1.585 \times 10^{-3}}{0.02} = 0.07925$$

$$\text{Percent dissociation} = \propto \times 100$$

$$= 0.07925 \times 100$$

$$= 7.925\ \%$$

Do you know ?

- *pH* is crucial for digestion of food and other biochemical reactions in our body.
- *pH* of gastric juice is about 2.
- *pH* of blood is maintained within range 7.36 to 7.42.
- Enzymes function effectively only at a certain *pH*. For example trypsin acts best for alkaline *pH*.

3.7 Hydrolysis of salts

3.7.1 Types of salts

These are of four types

I. Salts derived from **strong acid and strong base**. For example : NaCl, Na_2SO_4, $NaNO_3$, KCl, KNO_3.

II. Salts derived from **strong acids and weak bases**. For example : NH_4Cl, $CuSO_4$, NH_4NO_3, $CuCl_2$.

III. Salts derived from **weak acids and strong bases**. For example : CH_3COONa, KCN, Na_2CO_3.

IV. Salts derived from **weak acids and weak bases**. For example : CH_3COONH_4, NH_4CN.

3.7.2 Concept of hydrolysis : When a salt is dissociated in water, it dissociates completely into its constituent ions. The solvent water dissociates slightly as,

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Pure water is neutral and $[H_3O^{\oplus}] = [OH^{\ominus}]$. If the ions of the salt do not interact with water, the hydronium and hydroxyl ion concentrations remain equal and the solution is neutral. When one or more of the salt ions react with water, the equality of concentrations of $H_3O^{\oplus}$ and $OH^{\ominus}$ ions is disturbed. The solution, does not remain neutral and becomes acidic or basic depending on the type of the salt. Such a reaction between the ions of salt and the ions of water is called hydrolysis of salt. **Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).**

3.7.3 Salts of strong acids and strong bases

NaCl is a salt of strong acid HCl and a strong base NaOH. When it is dissolved in water, it dissociates completely into its ions.

$$NaCl\ (aq) \longrightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The ions $Na^{\oplus}$ and $Cl^{\ominus}$ have no tendency to react with water. This is because the possible products, NaOH and HCl of such reactions are

strong electrolytes and dissociate completely in aqueous solutions.

In other words,

$Na^{\oplus}(aq) + Cl^{\ominus}(aq) + H_2O \rightarrow HCl(aq) + NaOH(aq)$

(strong acid) (strong base)

[Possible products]

$HCl(aq) + NaOH(aq) + H_2O \rightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$

Thus the reactants and the products are the same. This implies that neither the cation nor anion of the salt reacts with water or there is no hydrolysis. Equality $H_3O^{\oplus} = OH^{\ominus}$ produced by ionization of water is not disturbed and solution is neutral. It may be concluded that salt of strong acid and strong base does not undergo hydrolysis.

3.7.4 Salts of strong acids and weak bases :

$CuSO_4$ is salt of strong acid H_2SO_4 and weak base $Cu(OH)_2$. When $CuSO_4$ is dissolved in water, it dissociates completely as,

$$CuSO_4(aq) \longrightarrow Cu^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$$

$SO_4^{2\ominus}$ ions of salt have no tendency to react with water because the possible product H_2SO_4 is strong electrolyte. The reaction of $Cu^{2\oplus}$ ions with $OH^{\ominus}$ ions form unionized $Cu(OH)_2$. The hydrolytic equilibrium for $CuSO_4$ is then written as,

$$Cu^{2\oplus}(aq) + 4H_2O(l) \rightleftharpoons Cu(OH)_2(aq) + 2H_3O^{\oplus}(aq)$$

Due to the presence of excess of $H_3O^{\oplus}$ ions, the resulting solution of $CuSO_4$ becomes acidic and turns blue litmus red.

Formation of sparingly soluble $Cu(OH)_2$ by hydrolysis makes the aqueous solution of $CuSO_4$ turbid. If H_2SO_4, that is $H_3O^{\oplus}$ ions are added, the hydrolytic equilibrium shifts to the left. A turbidity of $Cu(OH)_2$ dissolves to give a clear solution. To get clear solution of $CuSO_4$, the addition of H_2SO_4 would be required.

3.7.5 Salts of weak acids and strong bases

CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH, when dissolved in water, it dissociates completely.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

Water dissociates slightly as,

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Solution of CH_3COONa contains $Na^{\oplus}$, $H_3O^{\oplus}$, $CH_3COO^{\ominus}$, $OH^{\ominus}$. The $Na^{\oplus}$ ions of salt have no tendency to react with $OH^{\ominus}$ ions of water since the possible product of the reaction is NaOH, a strong electrolyte.

On the other hand the reaction of $CH_3COO^{\ominus}$ ions of salt with the $H_3O^{\oplus}$ ions from water produces unionized CH_3COOH.

$$CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$$

Thus, the hydrolytic equilibrium for CH_3COONa is,

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

As a result of excess $OH^{\ominus}$ ions produced the solution becomes basic. The solution of CH_3COONa is therefore basic.

Can you tell ?

Why an aqueous solution of NH_4Cl is acidic while that of HCOOK basic ?

Remember...

As a general rule the solutions of salts of strong acids and strong bases are neutral, the solutions of salts of strong acids and weak bases are acidic and the solutions of salts of strong bases and weak acids are basic.

3.7.6 Salts of weak acids and weak bases:

When salt BA of weak acid HA and weak base BOH is dissolved in water, it dissociates completely as

$$BA(aq) \longrightarrow B^{\oplus}(aq) + A^{\ominus}(aq)$$

The hydrolysis reaction involves the interaction of both the ions of the salt with water,

$B^{\oplus}(aq) + A^{\ominus}(aq) + H_2O \rightleftharpoons BOH + HA$

(weak base) (weak acid)

The solution may turn out acidic, basic or neutral depending on the relative strength of weak base and weak acid formed in the hydrolysis.

i. if, $K_a > K_b$, the solution will be acidic.

ii. if, $K_a < K_b$, the solution will be basic.

iii. if, $K_a = K_b$, the solution will be neutral.

i. Salt of weak acid and weak base for which $K_a > K_b$.

NH_4F is a salt of weak acid HF ($K_a = 7.2 \times 10^{-4}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$). Here, K_a is greater than K_b. The salt hydrolyses as

$NH_4^{\oplus}(aq) + F^{\ominus}(aq) + H_2O \rightleftharpoons NH_4OH(aq) + HF(aq)$

(weak base) (weak acid)

The acid HF is slightly stronger than base NH_4OH. The two ions react with water as

$NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$ ..... (3.19)

$F^{\ominus}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{\ominus}(aq)$ ..... (3.20)

The $NH_4^{\oplus}$ ions hydrolyse to a slightly greater extent than the $F^{\ominus}$ ions. That means the reaction produces more $H_3O^{\oplus}$ ions than the $OH^{\ominus}$ ions produced in reaction (3.20). In other words, $NH_4^{\oplus}$ ions are slightly stronger as acid than $F^{\ominus}$ ions as base. The solution of NH_4F is thus only slightly acidic and turns blue litmus red.

ii. Salt of weak acid and weak base for which $K_a < K_b$: NH_4CN is the salt of weak acid HCN ($K_a = 4.0 \times 10^{-10}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$) showing that $K_a < K_b$. When NH_4CN is dissolved in water, it hydrolyses as

$NH_4^{\oplus}(aq) + CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + HCN(aq)$

(weak base) (weak acid)

The base NH_4OH is stronger than the acid HCN. The ions of the salt react with water as,

$NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$ ..... (3.21)

$CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{\ominus}(aq)$ ..... (3.22)

The $CN^{\ominus}$ ions hydrolyse to a greater extent than $NH_4^{\oplus}$ ions, The reaction (3.22) produces more $OH^{\ominus}$ ions than the $H_3O^{\oplus}$ ions produced in reaction (3.21). The solution of NH_4CN is, basic and turns red litmus blue.

iii. Salt of weak acid and weak base for which $K_a = K_b$.

CH_3COONH_4 is a salt of weak acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and weak base, NH_4OH ($K_b = 1.8 \times 10^{-5}$).

When the salt CH_3COONH_4 is dissolved in water, it undergoes hydrolysis :

$CH_3COO^{\ominus}(aq) + NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$

(weak acid) (weak base)

The ions of the salt react with water as

i. $CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$

ii. $NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

As $K_a = K_b$, the relative strength of acid and base produced in hydrolysis is the same. Therefore, the solution is neutral. Hydrolysis of $NH_4^{\oplus}$ produces as many $H_3O^{\oplus}$ ions as that of $CH_3COO^{\ominus}$ produces $OH^{\ominus}$ ions.

3.8 Buffer solutions : Buffer solution is defined as a solution which resists drastic changes in pH when a small amount of strong acid or strong base or water is added to it.

Can you think ?

Home made jams and gellies without any added chemical preservative additives spoil in a few days whereas commercial jams and jellies have a long shelf life. Explain. What role does added sodium benzoate play?

3.8.1 Types of buffer solutions

There are two types of buffer solutions. Acidic buffer used to maintain an acidic pH, while basic buffer maintains alkaline pH.

a. Acidic buffer solution : A solution containing a weak acid and its salts with strong base is called an acidic buffer solution.

For example : A solution containing weak acid such as CH_3COOH and its salt such as CH_3COONa is an acidic buffer solution.

pH of acidic buffer is given by the equation

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]} \quad \ldots\ldots\ldots (3.23)$$

where $pK_a = -\log_{10}K_a$ $\ldots\ldots\ldots (3.24)$

and K_a is the dissociation constant of the acid.

b. Basic buffer solution : A solution containing a weak base and its salt with strong acid is the basic buffer solution.

For example : A solution containing a weak base such as NH_4OH and its salt such as NH_4Cl is a basic buffer solution.

The *pOH* of basic buffer is given by,

$$pOH = pK_b + \log_{10}\frac{[salt]}{[base]} \quad \ldots\ldots\ldots (3.25)$$

where $pK_b = -\log_{10}K_b$ $\ldots\ldots\ldots (3.26)$and K_b is the dissociation constant for the base. Equations (3.23), (3.24), (3.25) and (3.26) are known to **Henderson Hasselbalch equation**.

3.8.2 Buffer action : Let us consider sodium acetate - acetic acid buffer. Here sodium acetate is a strong electrolyte which dissociates completely in water producing large concentration of $CH_3COO^{\ominus}$ as follows :

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

On the other hand since the acetic acid is a weak acid, the concentration of undissociated CH_3COOH molecules is usually high. If a strong acid is added to this solution the added $H^{\oplus}$ ions will be consumed by the conjugate base $CH_3COO^{\ominus}$ present in large concentration. Similarly, if small amount of base is added, the added $OH^{\ominus}$ ions will be neutralized by the large concentration of acetic acid as shown in the following reactions :

$$\underset{\text{(large concentraion)}}{CH_3COO^{\ominus}(aq)} + \underset{\text{(added acid)}}{H^{\oplus}(aq)} \longrightarrow CH_3COOH(aq)$$

$$\underset{\text{(large concentraion)}}{CH_3COOH(aq)} + \underset{\text{(added base)}}{OH^{\ominus}(aq)} \longrightarrow CH_3COO^{\ominus}(aq) + H_2O(l)$$

The acid or base added thus can not change the $[H^{\oplus}]$ or $[OH^{\ominus}]$ concentrations and, *pH* of the buffer remains unchanged. Dilution does not have any effect on *pH* of buffer. This is because the concentration ratio term in Eq. (3.23) and Eq. (3.25) remains the same. The dilution does not change this ratio.

3.8.3 Properties of buffer solution

The *pH* of a buffer solution does not change appereciably

i. by addition of small amount of either strong acid or strong base, ii. on dilution or iii. when it is kept for long time.

Can you tell ?

It is enough to add a few mL of a buffer solution to maintain its *pH*. Which property of buffer is used here?

3.8.4 Applications of buffer solution

Buffer solution finds extensive applications in a variety of fields. Some of its applications are given.

i. In biochemical system : *pH* of blood in our body is maintained at 7.36 - 7.42 due to $(HCO_3^{\ominus} + H_2CO_3)$ buffer. A mere change of 0.2 *pH* units can cause death. The saline solution used for intravenous injection must contain

buffer system to maintain the proper *pH* of the blood.

ii. Agriculture : The soils get buffered due to presence of salts such as carbonate, bicarbonate, phosphates and organic acids. The choice of fertilizers depends upon *pH* of soil.

iii. Industry : Buffers play an important role in paper, dye, ink, paint and drug industries.

iv. Medicine : Penicillin preparations are stabilized by addition of sodium citrate as buffer. When citric acid is added to milk of magnesia ($Mg(OH)_2$), magnesium citrate is formed, which is a buffer.

v. Analytical chemistry : In qualitative analysis, a *pH* of 8 to 10 is required for precipitation of cations IIIA group. It is maintained with the use of ($NH_4OH + NH_4Cl$) buffer.

Problem 3.9 : Calculate the *pH* of buffer solution containing 0.05 mol NaF per litre and 0.015 mol HF per litre. [$K_a = 7.2 \times 10^{-4}$ for HF]

Solution : The *pH* of acidic buffer is given by Henderson-Hasselbalch equation

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]}$$

$\therefore pK_a = -\log_{10}K_a = -\log_{10} 7.2 \times 10^{-4}$

$= 4 - \log_{10} 7.2 = 4 - 0.8573 = 3.1427$

[salt] = 0.05 M, [acid] = 0.015M

Substitution in the above equation gives

$$pH = 3.1427 + \log_{10}\frac{0.05}{0.015}$$

$= 3.1427 + \log 3.33$

$= 3.1427 + 0.5224 = 3.6651 \approx 3.67$

Problem 3.10 : Calculate the *pH* of buffer solution composed of 0.1 M weak base BOH and 0.2 M of its salt BA. [$K_b = 1.8 \times 10^{-5}$ for the weak base]

Solution : *pOH* of basic buffer is given by Henderson-Hasselbalch equation

$$pOH = pK_b + \log_{10}\frac{[salt]}{[base]}$$

$\therefore pK_b = -\log_{10}K_b$

$= -\log_{10}(1.8 \times 10^{-5}) = 5 - \log_{10} 1.8$

$= 5 - 0.2553 = 4.7447$

[salt] = 0.02 M, [acid] = 0.1M

Substitution of these in the above equation gives

$pOH = 4.7447 + \log\frac{0.02}{0.1} = 4.7447 + \log 2$

$= 4.7447 + 0.3010 = 5.0457$

$pH = 14 - pOH = 14 - 5.0457$

$= 8.9543$

3.9 Solubility product

Can you recall ?

- What is solubility of a compound ?
- What is saturated solution ?
- What is meant by the sparingly soluble salt ?

Do you know ?

The process of dissolution and precipitation of sparingly soluble ionic compounds are of important in our everyday life, industry and medicine. Kidney stone is developed due to the precipitation of insoluble calcium oxalate, CaC_2O_4. The process of tooth decay occurs due to dissolution of enamel composed of hydroxyapatite, $Ca_5(PO_4)_3OH$ in acidic medium.

3.9.1 Solubility equilibria : Hereafter we confine our attention to sparingly soluble compounds that is, compounds those dissolve only slightly in water.

Suppose some powdered sparingly soluble salt such as AgCl is put into water and stirred vigorously. A very small amount of AgCl dissolves in water to form its saturated solution. Most of the salt remains undissolved. Thus, solid AgCl is in contact with its saturated solution. AgCl is a strong electrolyte. Hence the quantity of AgCl that dissolves in water dissociates completely into its constituent ions, $Ag^{\oplus}$ and $Cl^{\ominus}$. A dynamic equilibrium exists between undissolved solid AgCl and the dissolved ions, $Ag^{\oplus}$ and $Cl^{\ominus}$, in the saturated solution. This equilibrium, called solubility equilibrium, is represented as :

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The expression for its equilibrium constant is :

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{[AgCl]} \quad \ldots\ldots\ldots\ldots (3.27)$$

The concentration of undissolved solid AgCl is constant we may write

$$[AgCl] = \text{constant} = K'$$

Substituting in Eq. (3.27) we write

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{K'}$$

$$K \times K' = [Ag^{\oplus}][Cl^{\ominus}]$$

The product of $K \times K'$ is another constant and is called **solubility product**, that is the product of concentrations of ions in a saturated solution. It is denoted by K_{sp}.

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

For the general salt solubility equilibrium

$$B_xA_y(s) \rightleftharpoons xB^{y\oplus}(aq) + yA^{x\ominus}(aq)$$

The solubility product is

$$K_{sp} = [B^{y\oplus}]^x[A^{x\ominus}]^y \quad \ldots\ldots\ldots\ldots (3.28)$$

Thus, in the saturated solution of sparingly soluble salt the product of equilibrium concentrations of the constituent ions raised to the power equal to their respective coefficients in the balanced equilibrium expression at a given temperature is called solubility product.

Consider following examples.

i. $BaSO_4(s) \rightleftharpoons Ba^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$

$K_{sp} = [Ba^{2\oplus}][SO_4^{2\ominus}]$

ii. $CaF_2(s) \rightleftharpoons Ca^{2\oplus}(aq) + 2F^{\ominus}(aq)$

$K_{sp} = [Ca^{2\oplus}][F^{\ominus}]^2$

iii. $Bi_2S_3(s) \rightleftharpoons 2Bi^{3\oplus}(aq) + 3S^{2\ominus}(aq)$

$K_{sp} = [Bi^{3\oplus}]^2[S^{2\ominus}]^3$

iv. $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2\oplus}(aq) + 2PO_4^{3\ominus}(aq)$

$K_{sp} = [Ca^{2\oplus}]^3[PO_4^{3\ominus}]^2$

3.9.2 Relationship between solubility and solubility product : The solubility of a compound is the amount in grams that dissolves per unit volume (which may be 100 mL or 1L of its saturated solution).

Molar solubility : The number of moles of a compound that dissolve to give one litre of saturated solution is called its molar solubility.

$$\text{molar solubility (mol/L)} = \frac{\text{solubility in g/L}}{\text{molar mass in g/mol}}$$

Consider once again the solubility equilibrium for B_xA_y,

$$B_xA_y(s) \rightleftharpoons xB^{y\oplus}(aq) + yA^{x\ominus}(aq)$$

The solubility product is given by Eq. (3.28) :

$$K_{sp} = [B^{y\oplus}]^x[A^{x\ominus}]^y$$

If S is the molar solubility of the compound, the equilibrium concentrations of the ions in the saturated solution will be

$$[B^{y\oplus}] = xS \text{ mol/L}$$

$$[A^{x\ominus}] = xS \text{ mol/L}$$

From Eq. (3.28)

$$K_{sp} = [xS]^x[yS]^y = x^xy^yS^{x+y} \quad \ldots\ldots\ldots\ldots (3.29)$$

For example :

i. For AgBr,

$$AgBr(s) \rightleftharpoons Ag^{\oplus}(aq) + Br^{\ominus}(aq)$$

Here, $x = 1, y = 1$

$\therefore K_{sp} = S \times S = S^2$

ii. For PbI_2,

$PbI_2(s) \rightleftharpoons Pb^{2\oplus}(aq) + 2I^{\ominus}(aq)$

x = 1, y = 2

Therefore, $K_{sp} = (1)^1(2)^2S^{1+2} = 4S^3$

iii. $Al(OH)_3$,

$Al(OH)_3(s) \rightleftharpoons Al^{3\oplus}(aq) + 3OH^{\ominus}(aq)$

x = 1, y = 3

$K_{sp} = (1)^1(3)^3S^{1+3} = 27S^4$

Use your brain power

What is the relationship between molar solubility and solubility product for salts given below

i. Ag_2CrO_4 ii. $Ca_3(PO_4)_2$ iii. $Cr(OH)_3$.

3.9.3 Condition of precipitation : Ionic product (*IP*) of an electrolyte is defined in the same way as solubility product (K_{sp}). The only difference is that the ionic product expression contains concentration of ions under any condition whereas expression of K_{sp} contains only equilibrium concentrations. If,

a. $IP = K_{sp}$; the solution is saturated and solubility equilibrium exists.

b. $IP > K_{sp}$; the solution is supersaturated and hence precipitation of the compound will occur.

c. *If* $IP < K_{sp}$, the solution is unsaturated and precipitation will not occur.

Problem 3.11 : A solution is prepared by mixing equal volumes of 0.1M $MgCl_2$ and 0.3M $Na_2C_2O_4$ at 293 K. Would MgC_2O_4 precipitate out ? K_{sp} of MgC_2O_4 at 293 K is 8.56×10^{-5}.

Solution : When solution is prepared by mixing equal volumes, volume gets doubled and hence effective concentration of ions would be half of initial concentration,

$[Mg^{2+}] = \frac{0.1}{2} = 0.05$ mol/L

$[C_2O_4^{2-}] = \frac{0.3}{2}$ M = 0.15 mol/L

These ions would react to form sparingly soluble salt MgC_2O_4 in accordance with reaction

$Mg^{2\oplus}(aq) + C_2O_4^{2\ominus}(aq) \rightleftharpoons MgC_2O_4(s)$

Ionic product in the solution is given by

$[Mg^{2+}][C_2O_4^{2-}(aq)] = 0.05 \times 0.15$

$= 0.0075 = 7.5 \times 10^{-3}$

the K_{sp} value for MgC_2O_4 at 293 K is 8.56×10^{-5}. As ionic product is greater than K_{sp} precipitation will take place.

Problem 3.12 : The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol dm^{-3} and g dm^{-3}(Molar mass of AgBr = 187.8 g mol^{-1})

Solution : The solubility equilibrium of AgBr is :

$AgBr(s) \rightleftharpoons Ag^{\oplus}(aq) + Br^{\ominus}(aq)$

x = 1, y = 1

$K_{sp} = [Ag^{\oplus}][Br^{\ominus}] = S^2$

$S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}}$

$= 7.2 \times 10^{-7}$ mol dm^{-3}

The solubility in g dm^{-3} = molar solubility in mol dm^{-3} × molar mass g mol^{-1}

$S = 7.2 \times 10^{-7}$ mol $dm^{-3} \times 187.8$ g mol^{-1}

$= 1.35 \times 10^{-4}$ g dm^{-3}

Problem 3.13 : If 20.0 cm^3 of 0.050 M $Ba(NO_3)_2$ are mixed with 20.0 cm^3 of 0.020 M NaF, will BaF_2 precipitate ? K_{sp} of BaF_2 is 1.7×10^{-6} at 298 K.

Solution : Final volume of solution is

20 + 20 = 40 cm^3,

$[Ba(NO_3)_2] = \frac{0.050 \times 20}{40} = 0.025$ M

$[NaF] = \frac{0.020 \times 20}{40} = 0.010$M

Therefore $[Ba^{2\oplus}] = 0.025$ M and

$[F^{\ominus}] = 0.010$M

Hence ionic product of BaF_2 is

$IP = [Ba^{2\oplus}][F^{\ominus}]^2$

$= 0.025 \times (0.01)^2$

$= 2.5 \times 10^{-6}$

$K_{sp}(BaF_2) = 1.7 \times 10^{-6}$ Thus, $K_{sp} < IP$

Ionic product in the solution is greater than K_{sp}. Hence BaF_2 will precipitate from the solution.

3.10 Common ion effect :

Can you recall ?

Which reagents are used to precipitate (i) group II, (ii) group III B, (iii) group III A of basic radicals/ cations ?

Consider a solution of weak acid CH_3COOH and its soluble ionic salt CH_3COONa.

CH_3COOH is weak acid, dissociates only slightly in solution

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

CH_3COONa being a strong electrolyte dissociates almost completely in solution.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$$

Both the acid and the salt produce $CH_3COO^{\ominus}$ ions in solution. CH_3COONa dissociates completely. Therefore it provides high concentration of $CH_3COO^{\ominus}$ ions. According to Le-Chatelier principle, the addition of $CH_3COO^{\ominus}$ from CH_3COONa to the solution of CH_3COOH, shifts equilibrium of dissociation of CH_3COOH to left. Thus reverse reaction is favoured in which $CH_3COO^{\ominus}$ combines with $H^{\oplus}$ to form unionised CH_3COOH. Hence dissociation of CH_3COOH is supressed due to presence of CH_3COONa containing a common $CH_3COO^{\ominus}$ ion.

The common ion effect states that the ionisation of a weak electrolyte is supressed in presence of a strong electrolyte containing an ion common to the weak electrolyte.

Remember...

Common ion effect is a special case of Le-Chatelier's principle in which the stress applied to an equilibrium system is an increase in the concentration of one of the product (ions). The effect of this stress is reduced by shifting the equilibrium to the reactant side.

Can you tell ?

How does the ionization of NH_4OH suppressed by addition of NH_4Cl to the solution of NH_4OH ?

3.10.1 Common ion effect and solubility

Do you know ?

The hardness of water is due to presence of $Ca^{2\oplus}$ ions. It is surprising to know that $Ca^{2\oplus}$ ions can be removed by adding more $Ca^{2\oplus}$ ions in the form of lime $Ca(OH)_2$, to the hard water. The $OH^{\ominus}$ ions of lime react with $HCO_3^{\ominus}$ ions present in the hard water to form $CO_3^{2\ominus}$ ions.

$$OH^{\ominus}(aq) + HCO_3^{\ominus}(aq) \longrightarrow CO_3^{2\ominus}(aq) + H_2O(l)$$

Solubility product of $CaCO_3$ is very low ($K_{sp} = 4.5 \times 10^{-9}$). Addition of lime makes $IP >> Ksp$ which results in the precipitation of $CaCO_3$ and thereby removal of hardness.

The presence of a common ion also affects the solubility of a sparingly soluble salt. Consider, the solubility equilibrium of AgCl,

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The solubility product of AgCl is

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

Suppose $AgNO_3$ is added to the saturated solution of AgCl. The salt $AgNO_3$ being a strong electrolyte dissociates completely in the solution.

$$AgNO_3(aq) \longrightarrow Ag^{\oplus}(aq) + NO_3^{\ominus}(aq)$$

The dissociation of AgCl and $AgNO_3$ produce a common $Ag^{\oplus}$ ion. The concentration of $Ag^{\oplus}$ ion in the solution increases owing to complete dissociation of $AgNO_3$. According to Le-chatelier's principle the addition of $Ag^{\oplus}$ ions from $AgNO_3$ to the solution of AgCl shifts the solubility equilibrium of AgCl from right to left. The reverse reaction in which AgCl precipitates, is favoured until the solubility equilibrium is re-established. The value of K_{sp} however, remains the same since it is an equilibrium constant. The solubility of a sparingly soluble compound, thus decreases with the presence of a common ion in solution.

Exercises

1. Choose the most correct answer :

i. The *pH* of 10^{-8} M of HCl is
   a. 8 b. 7
   c. less than 7 d. greater than 7

ii. Which of the following solution will have pH value equal to 1.0 ?
   a. 50 mL of 0.1M HCl + 50mL of 0.1M NaOH
   b. 60 mL of 0.1M HCl + 40mL of 0.1M NaOH
   c. 20 mL of 0.1M HCl + 80mL of 0.1M NaOH
   d. 75 mL of 0.2M HCl + 25mLof 0.2M NaOH

iii. Which of the following is a buffer solution ?
   a. $CH_3COONa + NaCl$ in water
   b. $CH_3COOH + HCl$ in water
   c. $CH_3COOH + CH_3COONa$ in water
   d. $HCl + NH_4Cl$ in water

iv. The solubility product of a sparingly soluble salt AX is 5.2×10^{-13}. Its solubility in mol dm^{-3} is
   a. 7.2×10^{-7} b. 1.35×10^{-4}
   c. 7.2×10^{-8} d. 13.5×10^{-8}

v. Blood in human body is highly buffered at *pH* of
   a. 7.4 b. 7.0
   c. 6.9 d. 8.1

vi. The conjugate base of $[Zn(H_2O)_4]^{2\oplus}$ is
   a. $[Zn(H_2O)_4]^{2\ominus}NH_3$
   b. $[Zn(H_2O)_3]^{2\ominus}$
   c. $[Zn(H_2O)_3OH]^{\oplus}$
   d. $[Zn(H_2O)H]^{3\oplus}$

vii. For $pH > 7$ the hydronium ion concentration would be
   a. 10^{-7}M b. $< 10^{-7}$M
   c. $> 10^{-7}$M d. $\geq 10^{-7}$M

2. Answer the following in one sentence :

i. Why cations are Lewis acids ?

ii. Why is KCl solution neutral to litmus?

iii. How are basic buffer solutions prepared?

iv. Dissociation constant of acetic acid is 1.8×10^{-5}. Calculate percent dissociation of acetic acid in 0.01 M solution.

v. Write one property of a buffer solution.

vi. The *pH* of a solution is 6.06. Calculate its $H^{\oplus}$ ion concentration.

vii. Calculate the *pH* of 0.01 M sulphuric acid.

viii. The dissociation of H_2S is suppressed in the presence of HCl. Name the phenomenon.

ix. Why is it necessary to add H_2SO_4 while preparing the solution of $CuSO_4$?

x. Classify the following buffers into different types :

a. $CH_3COOH + CH_3COONa$

b. $NH_4OH + NH_4Cl$

c. Sodium benzoate + benzoic acid

d. $Cu(OH)_2 + CuCl_2$

3. Answer the following in brief :

i. What are acids and bases according to Arrhenius theory ?

ii. What is meant by conjugate acid-base pair?

iii. Label the conjugate acid-base pair in the following reactions

a. $HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$

b. $CO_3^{2\ominus} + H_2O \rightleftharpoons OH^{\ominus} + HCO_3^{\ominus}$

iv. Write a reaction in which water acts as a base.

v. Ammonia serves as a Lewis base whereas $AlCl_3$ is Lewis acid. Explain.

vi. Acetic acid is 5% ionised in its decimolar solution. Calculate the dissociation constant of acid

(Ans : 2.63×10^{-4})

vii. Derive the relation $pH + pOH = 14$.

viii. Aqueous solution of sodium carbonate is alkaline whereas aqueous solution of ammonium chloride is acidic. Explain.

ix. pH of a weak monobasic acid is 3.2 in its 0.02 M solution. Calculate its dissociation constant.

x. In NaOH solution $[OH^{\ominus}]$ is 2.87×10^{-4}. Calculate the *pH* of solution.

4. Answer the following :

i. Define degree of dissociation. Derive Ostwald's dilution law for the CH_3COOH.

ii. Define *pH* and *pOH*. Derive relationship between *pH* and *pOH*.

iii. What is meant by hydrolysis ? A solution of CH_3COONH_4 is neutral. why ?

iv. Dissociation of HCN is suppressed by the addition of HCl. Explain.

vi. Derive the relationship between degree of dissociation and dissociation constant in weak electrolytes.

vii. Sulfides of cation of group II are precipitated in acidic solution (H_2S + HCl) whereas sulfides of cations of group IIIB are precipitated in ammoniacal solution of H_2S. Comment on the relative values of solubility product of sulfides of these.

viii. Solubility of a sparingly soluble salt get affected in presence of a soluble salt having one common ion. Explain.

ix. The *pH* of rain water collected in a certain region of Maharashtra on particular day was 5.1. Calculate the $H^{\oplus}$ ion concentration of the rain water and its percent dissociation.

x. Explain the relation between ionic product and solubility product to predict whether a precipitate will form when two solutions are mixed?

Activity :

Take two test tubes and label them as A and B. Add Zinc filings in both the test tubes. In the test tube labelled A add 5 mL of 1M HCl and in test B 5 mL of acetic acid. Keep the test tubes on the stand. Note down your observations.

a. Do you see any effervescence coming from the two test tubes ?

b. Which gas is evolved ?

c. How do you identify the gas ?

d. What is the relative rate at which the gas is evolved in the two test tubes

e. Based on your observations comment on the strength of acids used.