CHEMISTRY

HIGHER SECONDARY - FIRST YEAR

VOLUME - I

REVISED BASED ON THE RECOMMENDATIONS OF THE
TEXT BOOK DEVELOPMENT COMMITTEE

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Untouchability is a sin
Untouchability is a crime
Untouchability is inhuman

TAMILNADU
TEXTBOOK CORPORATION
College Road, Chennai - 600 006

Following the progressing trend in chemistry, it enters into other branches of chemistry and answers for all those miracles that are found in all living organisms. The present book is written after following the revised syllabus, keeping in view with the expectations of National Council of Educational Research & Training (NCERT). The questions that are given in each and every chapter can be taken only as model questions. A lot of self evaluation questions, like, choose the best answer, fill up the blanks and very short answer type questions are given in all chapters. **While preparing for the examination, students should not restrict themselves, only to the questions/problems given in the self evaluation. They must be prepared to answer the questions and problems from the entire text.**

Learning objectives may create an awareness to understand each and every chapter.

Sufficient reference books are suggested so as to enable the students to acquire more informations about the concepts of chemistry.

Dr. V. BALASUBRAMANIAN
Chairperson
Syllabus Revision Committee (Chemistry)
& XI Std Chemistry Text Book Writing Committee

Unit 4 - Atomic Structure - I

Brief introduction of history of structure of atom - Defects of Rutherford's model and Niels Bohr's model of an atom - Sommerfeld's extension of atomic structure - Electronic configuration and quantum numbers - Orbitals-shapes of s, p and d orbitals. - Quantum designation of electron - Pauli's exclusion principle - Hund's rule of maximum multiplicity - Aufbau principle - Stability of orbitals - Classification of elements based on electronic configuration.

Unit 5 - Periodic Classification - I

Brief history of periodic classification - IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100 - Electronic configuration and periodic table - Periodicity of properties Anomalous periodic properties of elements.

Unit 6 - Group-1s Block elements

Isotopes of hydrogen - Nature and application - Ortho and para hydrogen - Heavy water - Hydrogen peroxide - Liquid hydrogen as a fuel - Alkali metals - General characteristics - Chemical properties - Basic nature of oxides and hydroxides - Extraction of lithium and sodium - Properties and uses.

Unit 7 - Group - 2s - Block elements

General characteristics - Magnesium - Compounds of alkaline earth metals.

Unit 8 -p- Block elements

General characteristics of p-block elements - Group-13. Boron Group - Important ores of Boron - Isolation of Born-Properties - Compounds of Boron-Borax, Boranes, diboranes, Borazole-preparation. properties - Uses of Boron and its compounds - Carbon group - Group -14 - Allotropes of carbon - Structural difference of graphite and diamond - General physical and chemical properties of oxides, carbides, halides and sulphides of carbon group - Nitrogen - Group-15 - Fixation of nitrogen - natural and industrial - HNO_3-Ostwald process - Uses of nitrogen and its compounds - Oxygen - Group-16 - Importance of molecular oxygen-cell fuel - Difference between nascent oxygen and molecular oxygen - Oxides classification, acidic basic, amphoteric, neutral and peroxide - Ozone preparation, property and structure - Factors affecting ozone layer.

Enthalpy of neutralisation - Various sources of energy-Non-conventional energy resources.

Unit 14 - Chemical Equilibrium - I

Scope of chemical equilibrium - Reversible and irreversible reactions - Nature of chemical equilibrium - Equilibrium in physical process - Equilibrium in chemical process - Law of chemical equilibrium and equilibrium constant - Homogeneous equilibria - Heterogeneous equilibria.

Unit 15 - Chemical Kinetics - I

Scope - Rate of chemical reactions - Rate law and rate determining step - Calculation of reaction rate from the rate law - Order and molecularity of the reactions - Calculation of exponents of a rate law - Classification of rates based on order of the reactions.

ORGANIC CHEMISTRY

Unit 16 - Basic Concepts of Organic Chemistry

Catenation - Classification of organic compounds - Functional groups - Nomenclature - Isomerism - Types of organic reactions - Fission of bonds - Electrophiles and nucleophiles - Carbonium ion Carbanion - Free radicals - Electron displacement in covalent bond.

Unit 17 - Purification of Organic compounds

Characteristics of organic compounds - Crystallisation - Fractional Crystallisation - Sublimation - Distillation - Fractional distillation - Steam distillation - Chromotography.

Unit 18 - Detection and Estimation of Elements

Detection of carbon and hydrogen - Detection of Nitrogen - Detection of halogens - Detection of sulphur - Estimation of carbon and hydrogen - Estimation of Nitrogen - Estimation of sulphur - Estimation of halogens.

Unit 19 - Hydrocarbons

Classification of Hydrocarbons - IUPAC nomenclature - Sources of alkanes - General methods of preparation of alkanes - Physical properties -

INORGANIC CHEMISTRY

1. CHEMICAL CALCULATION

OBJECTIVES

* *Know the method of finding formula weight of different compounds.*
* *Recognise the value of Avogadro number and its significance.*
* *Learn about the mole concept and the conversions of grams to moles.*
* *Know about the empirical and molecular formula and understand the method of arriving molecular formula from empirical formula.*
* *Understand the stoichiometric equation.*
* *Know about balancing the equation in its molecular form.*
* *Understand the concept of reduction and oxidation.*
* *Know about the method of balancing redox equation using oxidation number.*

1.1 Formula Weight (FW) or Formula Mass

The formula weight of a substance is the sum of the atomic weights of all atoms in a formula unit of the compound, whether molecular or not.

Sodium chloride, NaCl, has a formula weight of 58.44 amu (22.99 amu from Na plus 35.45 amu from Cl). NaCl is ionic, so strictly speaking the expression "molecular weight of NaCl" has no meaning. On the other hand, the molecular weight and the formula weight calculated from the molecular formula of a substance are identical.

Solved Problem

Calculate the formula weight of each of the following to three significant figures, using a table of atomic weight (AW): (a) chloroform $CHCl_3$ (b) Iron (III) sulfate $Fe_2(SO_4)_3$.

Solution

a. 1 x AW of C = 12.0 amu
1 x AW of H = 1.0 amu
3 x AW of Cl = 3 x 35.45 = 106.4 amu
Formula weight of $CHCl_3$ = 119.4 amu

i. How much does a given number of moles of a substance weigh?

ii. How many moles of a given formula unit does a given mass of substance contain.

Both of them can be known by using dimensional analysis.

To illustrate, consider the conversion of grams of ethanol, C_2H_5OH, to moles of ethanol. The molar mass of ethanol is 46.1 g/mol, So, we write

1 mol C_2H_5OH = 46.1 g of $C_2 H_5OH$

Thus, the factor converting grams of ethanol to moles of ethanol is 1mol C_2H_5OH/46.1g C_2H_5OH. To covert moles of ethanol to grams of ethanol, we simply convert the conversion factor (46.1 g C_2H_5OH/1 mol C_2H_5OH).

Again, suppose you are going to prepare acetic acid from 10.0g of ethanol, C_2H_5OH. How many moles of C_2H_5OH is this? you convert 10.0g C_2H_5OH to moles C_2H_5OH by multiplying by the appropriate conversion factor.

$$10.0\text{g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.1 \text{ g } C_2H_5OH} = 0.217 \text{ mol } C_2H_5OH$$

1.3.2 Converting Moles of Substances to Grams

Solved Problems

1. ZnI_2, can be prepared by the direct combination of elements. A chemist determines from the amounts of elements that 0.0654 mol ZnI_2 can be formed.

Solution

The molar mass of ZnI_2 is 319 g/mol. (The formula weight is 319 amu, which is obtained by summing the atomic weight in the formula) Thus

$$0.0654 \text{ mol } ZnI_2 \times \frac{319 \text{ g } ZnI_2}{1 \text{ mol } ZnI_2} = 20.9 \text{ gm } ZnI_2$$

Calculation of the Number of Molecules in a Given Mass

Solved Problem

How many molecules are there in a 3.46 g sample of hydrogen chloride, HCl?

Note: The number of molecules in a sample is related to moles of compound (1 mol HCl = 6.023 x 10^{23} HCl molecules). Therefore if you first convert grams HCl to moles, then you can convert moles to number of molecules).

Solution

$$3.46\,g\,HCl \times \frac{1\,mol\,HCl}{36.5\,g\,HCl} \times \frac{6.023 \times 10^{23}\,HCl\,molecules}{1\,mol\,HCl}$$

$$= \quad 5.71 \times 10^{22}\ HCl\ molecules$$

Problems for Practice

1. How many molecules are there in 55mg HCN?
2. Calculate the following
   a. Number of molecules in 43g CH_3
   b. Number of atoms in 22.0 g Br_2
   c. Number of atoms in 7.46 g Li

1.4 Calculation of Empirical Formula from Quantitative Analysis and Percentage composition

Empirical Formula

"An empirical formula (or) simplest formula for a compound is the formula of a substance written with the smallest integer subscripts".

For most ionic substances, the empirical formula is the formula of the compound. This is often not the case for molecular substances. For example, the formula of sodium peroxide, an ionic compound of Na^+ and O_2^{2-}, is Na_2O_2. Its empirical formula is NaO. Thus empirical formula tells you the ratio of numbers of atoms in the compound.

Steps for writing the Empirical formula

The percentage of the elements in the compound is determined by

suitable method) by the empirical formula mass and find out the value of n which is a whole number.

iv. Multiply the empirical formula of the compound with n, so as to find out the molecular formula of the compound.

Solved Problem

1. A compound on analysis gave the following percentage composition C = 54.54%, H, 9.09% 0 = 36.36. The vapour density of the compound was found to be 44. Find out the molecular formula of the compound.

Solution

Calculation of empirical formula

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
C	54.54	$\frac{54.54}{12} = 4.53$	$\frac{4.53}{2.27} = 2$	2
H	9.09	$\frac{9.09}{1} = 9.09$	$\frac{9.09}{2.27} = 4$	4
O	36.36	$\frac{36.36}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

Empirical formula is $C_2 H_4 O$.

Calculation of Molecular formula

Empirical formula mass = 12 x 2 + 1 x 4 + 16 x 1 = 44

Molecular mass = 2 x Vapour density

= 2 x 44 = 88

$$n = \frac{\text{Molecular mass}}{\text{Empirical Formula mass}} = \frac{88}{44} = 2$$

Molecular formula = Empirical formula x n

$$H_2 + Br_2 \rightarrow HBr$$

This is the skeletal equation. The number of atoms of hydrogen on the left side is two but on the right side it is one. So the number of molecules of HBr is to be multiplied by two. Then the equation becomes

$$H_2 + Br_2 \rightarrow \quad 2HBr$$

This is the balanced (or) stoichiometric equation.

Example 2

Potassium permanganate reacts with HCl to give KCl and other products. The skeletal equation is

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$

If an element is present only one substance in the left hand side of the equation and if the same element is present only one of the substances in the right side, it may be taken up first while balancing the equation.

According to the above rule, the balancing of the equation may be started with respect to K, Mn, O (or) H but not with Cl.

There are

	L.H.S	**R.H.S**
K =	1	1
Mn =	1	1
O =	4	1

So the equation becomes

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + 4H_2O + Cl_2$$

Now there are eight hydrogen atoms on the right side of the equation, we must write 8 HCl.

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + Cl_2$$

Of the eight chlorine atoms on the left, one is disposed of in KCl and two in $MnCl_2$ leaving five free chlorine atoms. Therefore, the above equation becomes

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + 5/2\ Cl_2$$

Equations are written with whole number coefficient and so the

10 kg of $CaCO_3$ produces = $\frac{44}{100 \times 10^{-3}} \times 10$

= 4.4 kg of CO_2

Example 2

Calculate the mass of oxygen obtained by complete decomposition of 10kg of pure potassium chlorate (Atomic mass K=39, O=16 and Cl = 35.5)

$$2KClO_3 \rightarrow 2\ KCl + 3O_2$$

Molecular mass of $KClO_3$ = 39+35.5+48=122.5

Molecular Mass of O_2 = 16 + 16 = 32.

According to the Stoichiometric equation written above (2 x 122.5) x 10^{-3} kg of $KClO_3$ on heating gives (3 x 32) x 10^{-3} kg of oxygen.

10kg of $KClO_3$ gives = $\frac{3 \times 32 \times 10^{-3}}{2 \times 122.5 \times 10^{-3}} \times 10$

= 3.92 kg of O_2

Example 3

Calculate the mass of lime that can be prepared by heating 200 kg of limestone that is 90% pure $CaCO_3$

$CaCO_3 \rightarrow CaO + CO_2$

100 kg x 10^{-3} 56 kg x 10^{-3}

200 kg of 90% pure $CaCO_3$ = $200 \times \frac{90}{100}$

= 180 kg pure $CaCO_3$

100x10^{-3} kg of pure $CaCO_3$ on heating gives 56 x 10^{-3} kg of Ca0

180 kg of $CaCO_3$ gives on heating = $\frac{56 \times 10^{-3} \times 180}{100 \times 10^{-3}}$

= 100.8 kg CaO

1.7 Methods of Expressing the concentration of solution

Example

A 0.1M solution of Sugar, $C_{12}H_{22}O_{11}$ (mol.mass = 342), means that 34.2 g of sugar is present in one litre (1000 cm^3) of the solution.

3. Normality

Normality of a solution is defined as the number of gram equivalents of the solute dissolved per litre of the given solution.

$$\text{Normality} = \frac{\text{Number of gram-equivalents of solute}}{\text{Volume of Solution in litre}}$$

If X grams of the solute is present in V cm^3 of a given solution, then,

$$\text{Normality} = \frac{X}{\text{Eq.mass}} \times \frac{1000\ \text{mL}}{V}$$

Normality is represented by the symbol N. Normality can also be calculated from strength as follows:

$$\text{Normality} = \frac{\text{Strength in grams per litre}}{\text{Eq.mass of the solute}}$$

Example

A 0.1N (or decinormal) solution of H_2SO_4 (Eq.mass = 49), means that 4.9 g of H_2SO_4 is present in one litre (1000 cm^3) of the solution.

4. Molality (m)

Molality of a solution is defined as the number of gram-moles of solute dissolved in 1000 grams (or 1 kg) of a Solvent. Mathematically,

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kilograms}}$$

"If X grams of the solute is dissolved in b grams of the solvent", then

Molecular mass = 2 x vapour density

$$\text{Vapour density} = \frac{\text{Molecular mass}}{2}$$

Problem

In the determination of molecular mass by Victor-Meyer's Method 0.790 g of a volatile liquid displaced $1.696 \times 10^{-4} m^3$ of moist air at 303 K and at 1×10^5 Nm^{-2} pressure. Aqueous tension at 303 K is 4.242×10^3 Nm^{-2}. Calculate the molecular mass and vapour density of the compound.

Mass of the organic compound = 0.79 g

Volume of Vapour = $V_1 = 1.696 \times 10^{-4} m^3$

Volume of air displaced = Volume of vapour

P_1 = (atmospheric pressure - aqueous tension)

= $(1.0 \times 10^5) - (4.242 \times 10^3) = 0.958 \times 10^5$ Nm^{-2}

T_1 = 303 K

Initial Values	**Values at S.T.P**
$V_1 = 1.696 \times 10^{-4}$ Nm^{-2}	V_o = ?
$P_1 = 0.958 \times 10^{-5} \times 10^5$ Nm^{-2}	$P_o = 1.013 \times 10^5$ Nm^{-2}
T_1 = 303 K	T_0 = 273 K

$$\frac{P_1V_1}{T_1} = \frac{P_0V_0}{T_0}$$

$$V_0 = \frac{P_1V_1T_0}{P_0T_1}$$

$$V_0 = \frac{0.958 \times 10^5 \times 1.696 \times 10^{-4}}{1.013 \times 10^5} \times \frac{273}{303}$$

concept, Avogardo number and its significance are dealt. The application of the various concepts are explained by solving problems. By knowing the percentage composition of elements in a compound, empirical formula and molecular formula can be calculated.

It is important to write the stoichiometric equation. So, the method of balancing the any equation explained and given or practice. And also the method of balancing redox equation using oxidation number is dealt.

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2. University General Chemistry
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   McMillan Indian Limited, Reprint-2002.
3. Heinemann Advanced Science Chemistry – Second Edition
   Ann and Patrick Fullick 2000
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4. Inorganic Chemistry, P.L. Soni.

earth's crust and the process of taking out the ores from the earth crust is called **mining**.

In the combined state ores are generally found in the form of oxides, sulphides, carbonates, sulphates, chlorides and silicates. The important ores are given in Table 2.1.

Table 2.1 Classification of ores

Ore	Ore or Mineral	Composition	Metal Present
Oxide ores	Bauxite	$Al_2O_3.2H_2O$	Al
	Cuprite	Cu_2O	Cu
	Haematite	Fe_2O_3	Fe
	Zincite	ZnO	Zn
	Tinstone or Casseterite	SnO_2	Sn
	Pyrolusite	MnO_2	Mn
	Pitch Blende	U_3O_8	U
Sulphide ores	Copper Pyrites	Cu_2S, Fe_2S_3 or $Cu_2S.FeS_2$	Cu
	Copper Glance	Cu_2S	Cu
	Zinc Blende	ZnS	Zn
	Cinnabar	HgS	Hg
	Galena	PbS	Pb
	Argentite or Silver Glance	Ag_2S	Ag
Carbonate ores	Magnesite	$MgCO_3$	Mg
	Dolomite	$CaCO_3.MgCO_3$	Mg
	Calamine	$ZnCO_3$	Zn
	Malachite	$CuCO_3.Cu(OH)_2$	Cu
	Limestone	$CaCO_3$	Ca

(4) If an electron jumps from one stationary state to another, it will absorb or emit radiation of a definite frequency giving a spectral line of that frequency which depends upon the initial and final levels. When an electron jumps back to the lower energy level, it radiates same amount of energy in the form of radiation.

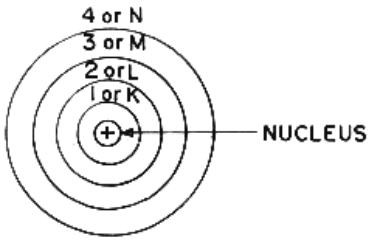


Fig. 3.2 Bohr's orbits

Limitation of Bohr's Theory

(i) According to Bohr, the radiation results when an electron jumps from one energy orbit to another energy orbit but how this radiation occurs is not explained by Bohr.

(ii) Bohr's theory had explained the existence of various lines in H-spectrum, but it predicted that only a series of lines exist. At that time this was exactly what had been observed. However, as better instruments and techniques were developed, it was realized that the spectral line that had been thought to be a single line was actually a collection of several lines very close together (known as fine spectrum). Thus for example, the single H∞-spectral line of Balmer series consists of many lines very close to each other.

(iii) Thus the appearance of the several lines implies that there are several energy levels, which are close together for each quantum number n. This would require the existence of new quantum numbers.

(iv) Bohr's theory has successfully explained the observed spectra for hydrogen atom and hydrogen like ions (e.g. He^{+}, Li^{2+}, Be^{3+} etc.), it can not explain the spectral series for the atoms having a large number of electrons.

number, the spin quantum number, (*s*) is necessary to describe an electron completely.

4. Spin quantum number (*s*)

The electron in the atom rotates not only around the nucleus but also around its own axis and two opposite directions of rotation are possible (clock wise and anticlock wise). Therefore the spin quantum number can have only two values +1/2 or –1/2. For each values of m including zero, there will be two values for *s*.

To sum up, the four quantum numbers provide the following informations:

1. n identifies the shell, determines the size of the orbital and also to a large extent the energy of the orbit.
2. There are n subshells in the n^{th} shell. *l* identifies the subshell and determines the shape of the orbital. There are (2*l*+1) orbitals of each type in a subshell i.e., one s orbital (*l*=0), three p orbitals (*l*=1), and five d orbitals (*l*=2) per subshell. To some extent *l* also determines the energy of the orbital in a multi-electron atom.
3. m_l designates the orientation of the orbital. For a given value of *l*, m_l has (2*l*+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.
4. m_s refers to orientation of the spin of the electron.

Example 1

What is the total number of orbitals associated with the principal quantum number n=3 ?

Solution

For n = 3, the possible values of *l* are 0,1 and 2. Thus, there is one 3s orbital (n = 3, *l* = 0 and m_l = 0); there are three p orbitals (n = 3, *l* = 1 and m_l = -1, 0, 1) there are five 3d orbitals (n = 3, *l* = 2, m_l = -2, -1, 0, 1, 2).

Therefore, the total number of orbitals is 1+3+5 = 9.

Example 2

Using s, p, d, f notations, describe the orbital with the following quantum numbers (a) n=2, l = 1 (b) n = 4, l = 0 (c) n = 5, l = 3 (d) n = 3, l = 2.

Solution

	n	l	orbital
(a)	2	1	2p
(b)	4	0	4s
(c)	5	3	5f
(d)	3	2	3d

3.4 Shapes or boundary surfaces of Orbitals

***s*-orbitals:** For s-orbital l = 0 and hence, m can have only one value, i.e., m = 0. This means that the probability of finding the electron in s-orbital is the same in all directions at a particular distance. In other words s-orbitals are spherically symmetrical.

The electron cloud picture of 1s orbital is spherical. The *s*-orbitals of higher energy levels are also spherically symmetrical. However, they are more diffused and have spherical shells within them where probability of finding the electron is zero. These are called nodes. In 2*s*-orbital there is one spherical node. In the ns orbital, number of nodes are (n-1).

***p*-orbitals:** For p-orbitals l = 1 and hence 'm' can have three possible values +1, 0, -1. This means that there are three possible orientations of electron cloud in a *p*-sub-shell. The three orbitals of a *p*-sub-shell are designated as p_x, p_y and p_z respectively along x-axis, y-axis and z-axis respectively. Each *p*-orbital has two lobes, which are separated by a point of zero probability called node. Each *p*-orbital is thus dumb bell shaped.

In the absence of magnetic field these three *p*-orbitals are equivalent in energy and are, therefore, said to be three-fold degenerate or triply degenerate. In the presence of an external magnetic field, the relative energies of the three *p* orbitals vary and depend on their orientation or

C. Write in one or two sentence

1. What is the charge of an electron, proton and a neutron ?
2. What is atomic number?
3. What is the maximum number of electrons that an orbital can have?
4. How many orbitals are there in the second orbit? How are they designated?
5. Sketch the shape of s and p-orbital indicating the angular distribution of electrons.
6. What are the charge and mass of an electron?
7. What is an orbital?
8. Give the order of filling of electrons in the following orbitals 3p, 3d,4p, 3d and 6s.
9. What is meant by principal quantum number?
10. How many protons and neutrons are present in $^{18}_{8}O$?
11. What are the particles generally present in the nuclei of atoms?
12. The atomic mass of an element is 24 and its atomic number is 12. Show how the atom of the element is constituted?
13. How will you experimentally distinguish between a ray of neutron and ray of proton?
14. What is the principal defect of Bohr atom model?
15. Write the complete symbol for : (a) The nucleus with atomic number 56 and mass number 138 ; (b) The nucleus with atomic number 26 and mass number 55 ; (c) The nucleus with atomic number 4 and mass number 9.
16. An atomic orbital has n = 3. What are the possible values of *l* ?
17. An atomic orbital has *l*= 3. What are the possible values of m?
18. Give the electronic configuration of chromium. (Z=24).
19. Which energy level does not have p-orbital?

4.3 Electronic configuration and periodic table

There is a close connection between the electronic configuration of the elements and the long form of the Periodic Table. We have already learnt that an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as the **Shell**. The electronic configuration of elements can be best studied in terms of variations in periods and groups of the periodic table.

(a) Electronic Configuration in periods

Each successive period in the periodic table is associated with the filling up of the next higher principal energy level (n=1, n=2,etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. The first period starts with the filling of the lowest level (1s) and has thus the two elements-hydrogen ($1s^1$) and helium ($1s^2$), when the first shell (K) is completed. The second period starts with lithium and the third electron enters the 2s orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron the 2p orbitals are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period (n=3) begins at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period (n=4) starts at potassium with the filling up of 4s orbital. Now you may note that before the 4p orbital is filled, filling up of 3d orbitals becomes energetically favourable and we come across the so-called 3d Transition Series of elements. The fourth period ends at krypton with the filling up of the 4p orbitals. Altogether we have 18 elements in this fourth period. The fifth period (n=5) beginning with rubidium is similar to the fourth period and contains the 4d transition series starting at yttrium (Z=39). This period ends at xenon with filling up of the 5p orbitals. The sixth period (n=6) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbitals, in that order. Filling up of the 4f orbitals begins with cerium (Z=58) and ends at lutetium (Z=71) to give the 4f-inner transition series, which is called the **Lanthanoid Series**. The seventh period (n=7) is similar to the sixth

1. **Burning in oxygen:** Like hydrogen, it is combustible and burns in oxygen or air to give deuterium oxide which is also known as heavy water.

$$2\,D_2 + O_2 \longrightarrow 2D_2O.$$

2. **Reaction with halogens:** Like hydrogen, it combines with halogens under suitable conditions to form their deuterides.

$$D_2 + Cl_2 \xrightarrow{\text{in light}} \underset{\text{Deuterium chloride}}{2\,DCl}$$

$$D_2 + F_2 \xrightarrow{\text{in dark}} \underset{\text{Deuterium fluoride}}{D_2F_2}$$

3. **Reaction with nitrogen:** Like hydrogen, it combines with nitrogen in the presence of a catalyst to form nitrogen deuteride which are also known as heavy ammonia or deutero ammonia.

$$3D_2 + N_2 \longrightarrow 2ND_3$$

4. **Reaction with metals:** Like hydrogen, it reacts with alkali metals at high temperatures (633K) to form deuterides

$$2\,Na + D_2 \longrightarrow 2\,NaD$$

5. **Addition reactions:** Like hydrogen, it gives addition reactions with unsaturated compounds. For example, a mixture of deuterium and ethylene when passed over heated nickel, gives Ethylene deuteride which is saturated hydrocarbon like ethane.

$$C_2H_4 + D_2 \xrightarrow[535\ K]{Ni} CH_2D\text{-}CH_2D$$

6. **Exchange reactions:** Deuterium and hydrogen atoms undergo ready exchange with H_2, NH_3, H_2O and CH_4 deuterium slowly exchanges their hydrogens partially or completely at high temperatures.

$$H_2 + D_2 \rightleftharpoons 2\,HD$$

$$2NH_3 + 3D_2 \rightleftharpoons 2ND_3 + 3H_2$$

(ii) Boiling point of para hydrogen 20.26K while that of ordinary hydrogen is 20.39K.

(iii) The vapour pressure of liquid para hydrogen is higher than that of ordinary liquid hydrogen.

(iv) The magnetic moment of para hydrogen is zero since the spins neutralise each other while in the case of ortho , it is twice than that of a proton.

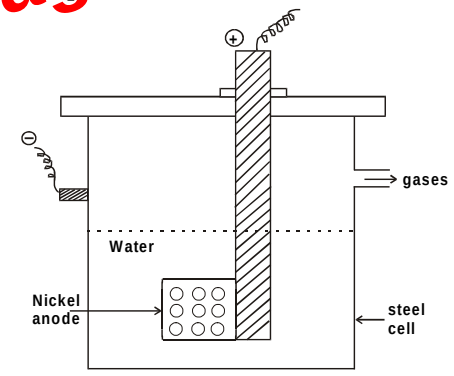
(v) Para hydrogen possesses a lower internal molecular energy than ortho form.

5.2 Heavy water

It is also called as deuterium oxide. The oxide of heavy hydrogen (deuterium) is called heavy water. Heavy water was discovered by Urey in 1932. By experimental data he showed that `ordinary water', H_2O contains small proportion of heavy water, D_2O (about 1 part in 5000).

Preparation: The main source of heavy water is the ordinary water from which it is isolated. Generally it is prepared by exhaustive electolysis.

Principle: The heavy water is isolated either by prolonged electrolysis or by fractional distillation of water containing alkali. Taylor, Eyring and Frost in 1933 formulated the electrolysis of water in seven stages using N/2-NaOH solution and steel nickel electrodes.



The cell consists of a steel cell 18 inches long and 4 inches in diameter. The cell itself serves as the cathode while the anode consists of a cylindrical sheet of nickel with a number of holes punched in it. A large number of

8. H_2O_2 is a powerful _____ agent
   (a) dehydrating (b) oxidising (c) reducing (d) desulphurising
9. _____ is used as a propellant in nucleus
   (a) H_2O_2 (b) D_2O (c) ND_3 (d) $CH_2 = CH_2$
10. The oxidation state of alkali metals is
   (a) +2 (b) 0 (c) +1 (d) +3
11. When heated in bunsen flame, lithium gives _____ colour
   (a) yellow (b) blue (c) lilac (d) crimson red
12. On moving down the group, density of the alkali metals
   (a) increases (b) decreases
   (c) increases and then decreases (d) decreases and then increases
13. If the element can lose an electron readily, they are said to be
   (a) electronegative (b) electropositive
   (c) electronative (d) electrovalent

B. Fill in the blanks

1. The first element in the periodic table is _____.
2. _____ is the common formd of hydrogen.
3. The half-life of tritium is _____.
4. Deuterium reacts with ammonia to form _____.
5. The rare isotope of hydrogen is _____.
6. _____ is employed in nuclear reactor to slow down the speed of fast moving neutrons.
7. The magnetic moment of para hydrogen is _____.
8. Deuterium with salt and other compounds forms _____.
9. Hydrogen peroxide was first prepared by _____ in _____.
10. Pure H_2O_2 is _____.
11. The Arabic word `Alquili' means _____.
12. The electronic configuration of potassium is _____.
13. All alkali metals have _____ melting and boiling points.
14. On moving down the group of alkali metals, ionization energy _____.
15. _____ is the lightest of all solid elements.

C. Write in one or two sentences

1. What are isotopes? Mention the isotopes of hydrogen.
2. Write a short note on tritium.
3. How does deuterium react with nitrogen?
4. How does deuterium react with metals?
5. Mention the uses of deuterium.

completed s-subshell. Thus, the outer electronic configuration of each element is ns^2 where n is the number of the valence shell. It can be expected that the two electrons can be easily removed to give the inert gas electronic configuration. Hence these elements are all bivalent and tend to form ionic salts. Thus ionic salts are less basic than group 1. Due to their alike electronic structure, these elements resemble closely in physical and chemical properties.

The variation in physical properties are not as regular as for the alkalimetals because the elements of this group do not crystallise with the same type of metallic lattice.

These elements have been sufficiently soft yet less than the alkalimetals as metallic bonding in these elements has been stronger than in first group alkali elements.

Beryllium is unfamiliar, partly because it is not very abundant and partly because it is difficult to extract. Magnesium and calcium are abundant and among the eight most common elements in the earth's curst. Strontium and barium are less abundant but are well known, while radium is extremely scarce and its radioactivity is more important than its chemistry.

Metallic properties

The alkaline earth metals are harder than the alkali metals. Hardness decreases, with increase in atomic number. They show good metallic lustre and high electrical as well as thermal conductivity because the two s-electrons can easily move through the crystal lattice.

Melting and Boiling Points

Both melting and boiling points do not show regular trends because atoms adopt different crystal structures. They possess low melting and boiling points. These are, however, higher than those of alkali metals because the number of bonding electrons in these elements is twice as great as group 1 elements.

Atomic radius

The atoms of these elements are somewhat smaller than the atoms of the corresponding alkali metals in the same period. This is due to higher

The electrolysis of the fused mass is carried out in an atmosphere of coal gas in air tight iron cell which can hold 6-7 tonnes of the electrolyte. The temperature of the elctrolyte bath is maintained at 970K. The iron cell itself acts as a cathode unlike the anode consists of a carbon or graphite rod surrounded by a porcelain tube through which the liberated chlorine escapes. Molten magnesium being lighter than the electrolyte, rises to the surface and is periodically removed with perforated ladle. The electrolysis is carried out in an atmosphere of coal gas so as to avoid the oxidation of molten magnesium. The metal thus obtained is 99.9% pure. It may be further purified by remelting with a flux of anhydrous magnesium chloride and sodium chloride.

Physical

Pure magnesium metal is a relatively active silvery white metal. At slightly below its melting point, it is malleable and ductile and can be drawn into wire or rolled into ribbon in which form it is generally sold. It is a very light metal.

Chemical Properties

1. **Action of Air :** It does not tarnish in dry air but a layer of white oxide is formed on its surface in moist air.
2. **With air on burning :** It burns in air or oxygen with a dazzling light rich in ultraviolet rays, forming magnesium oxide and magnesium nitride.

$$2Mg + O_2 \rightarrow 2Mg\,O$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

3. **With CO_2**

It continues to burn in CO_2,

$$2\,Mg + CO_2 \rightarrow 2\,MgO + C$$

4. **Action of Water**

When heated with steam it burns brilliantly producing magnesium oxide and hydrogen.

$$Mg + \underset{\text{steam}}{H_2O} \rightarrow MgO + H_2$$

5. Action of Acids

Dilute HCl or H_2SO_4 gives hydrogen with magnesium. With dilute HNO_3, part of the hydrogen liberated is oxidised by nitric acid, which itself is reduced to a variety of products depending upon the concentration. With concentrated HNO_3, it gives ammonium nitrate.

$$4Mg + 10HNO_3 \rightarrow 4\,Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$

6. Displacement of Metals

It is a strongly electropositive metal and hence Mg displaces nearly all the metals from the solutions of their salts eg.

$$Mg + 2AgNO_3 \rightarrow Mg(NO_3)_2 + 2Ag$$

7. Reducing Action

Mg has great affinity for oxygen and it liberates sodium, potassium, boron and silicon from their oxides at high temperatures.

$$K_2O + Mg \rightarrow MgO + 2K$$

$$B_2O_3 + 3Mg \rightarrow 3MgO + 2B$$

Uses of Magnesium

1. In flashlight photography, pyrotechnics and in fireworks.
2. As a reducing agent in the preparation of boron and silicon and deoxidiser in metallurgy.

6.3 Compounds of alkaline earth metals

Magnesium sulphate, epsom slat, $MgSO_4.7H_2O$

It is prepared by dissolving magnesium oxide or carbonate in dilute sulphuric acid.

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

Uses

1) As a purgative
2) In dyeing and tanning processes and in dressing cotton goods.
3) Platinised $MgSO_4$ is used as a catalyst.

C. Match the following

1.	Magnetite	$CaSO_4 . 2H_2O$
2.	Dolamite	$Mg Cl_2 . KCl . 6H_2O$
3.	Epsom salt	$MgCO_3$
4.	Carnallite	$MgCO_3 . CaCO_3$
5.	Gypsum	$MgSO_4 . 7H_2O$

Problem

An element occupies group number 2 and period number 3. This element reacts with oxygen and nitrogen to form compound A and B. It is a strong electropositive metal so it displaces Ag from $AgNO_3$ solution. With concentrated nitric acid, it forms compound C. Identify the element, compound A, B and C.

D. Write in one or two sentence

1. Why the oxides of Group 2 metals have high melting points?
2. Why there is increase in the ionization potential for forming M^{3+} ion for group 2 metals?
3. Why the ionization potential of M^{2+} is not very much greater than M^{+}?
4. Why a precipitate of $Mg(OH)_2$ is not formed when aqueous ammonia, NH_4OH is added to a solution of $MgCl_2$?
5. List the carbonates and hydroxide of alkaline earth metals in order of their increasing stability and their solution.
6. Why do beryllium halides fume in air?
7. Why group 2 elements are harder than alkali metals?
8. Beryllium halides are covalent whereas magnesium halides are ionic. Why?
9. Why are monoxides of alkaline earth metals are very stable?
10. The basic strength of the oxides of group 2 elements increases from Be to Ba. Why?

D. Explain briefly on the following

1. What are alkaline earth metals? Why are they called so?
2. In what respects Be and Mg differ from all the other metals of group 2.

3. How can you explain the anomalous behaviour of beryllium.
4. How does magnesium occur in nature? How is the metal extracted from its Ore?
5. In the light of metallic bonding account for the following properties of group 2 elements.
   a. These are harder than alkali metals
   b. These are good conductors of heat and electricity.
6. Why the first ionization energy of alkaline earth metals higher than that of Ist group.
7. Mention the uses of plaster of Paris.
8. How is plaster of paris prepared?
9. How is $MgSO_4$ prepared?
10. Mention the uses of Magnesium?

SUMMARY

The second group of periodic table is known as alkaline earth metals. Like alkali metals they are reactive. The physical properties and chemical of these elements are explained.

The metallurgy of Mg, its physical and chemical properties are explained in detail. Some compounds of alkaline earth metals such as Epsom salt, calcium sulphate, quick lime, gypsum and plaster of paris are dealt.

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7. *p*-BLOCK ELEMENTS

OBJECTIVES

After studying this unit, you will be able to

* *Understand the nature and properties of p-block elements.*
* *Know the important ores of boron.*
* *Understand the isolation of boron from its ores.*
* *Understand the preparation, properties and uses of boron compounds.*
* *Learn about the allotropes of carbon.*
* *Understand the structure of graphite and diamond and the difference between them.*
* *Acquire knowledge about oxides, carbides, halides and sulphides of carbon group.*
* *Learn about fixation of nitrogen.*
* *Understand the preparation, properties and structure of nitric acid.*
* *Recognise the uses of nitrogen and its compounds.*
* *Know the importance of molecular oxygen and the differences between nascent oxygen and molecular oxygen.*
* *Realise the importance of ozone to life.*

7.1 General Characteristics

The elements belonging to the group 13 to 18 of the periodic table, in which p-orbitals are progressively filled are collectively known as p-block elements.

In all these elements while s-orbitals are completely filled, their p-orbitals are incomplete. These are progressively filled by the addition of one electron as we move from group 13 (ns^2np^1) to group 17 (ns^2np^5). In group 18 (ns^2np^6) both s and p-orbitals are completely filled.

p-block elements show a variety of oxidation state both positive and negative. As we go down the group, two electrons present in the valence `s' orbital become inert and the electrons in the `p' orbital are involved in chemical combination. This is known as `inert pair effect'.

The inert pair effect is really a name, not an explanation. A full explanation involves the decreasing strength of the M-X bond going down the group (for covalent compounds) or the decreasing lattice energies of compounds containing the M^{4+} ion (for ionic compounds). In this way the energy input needed to form compounds of the formula MX_4 are less likely to be balanced by the energy released when the four M-X bonds are formed, so the equilibrium favours the left hand side.

$$MX_2 + X_2 \rightarrow MX_4$$

The existence of a positive oxidation state corresponding to the group number and of another state two units lower is an illustration of the inert pair effect, the term referring to the valence `s' electrons, used in bonding in the higher oxidation state but not in the lower.

With the increase in atomic mass, the ionic character of bonds of the compounds of the group 13 (IIIA) elements increases, and some of the heavier metal ions do exist in the +3 oxidation state in aqueous solution. The stability of such compounds with the +3 oxidation state is, however, lower than those with the +1 oxidation state in the case of heavier members of this group. Thus thallium in +1 oxidation state is more stable than in +3 state. This is because, the `s' electrons in the ns sub-shell do not prefer to form bonds.

This inertness is found only, i) when the `s' electrons are in the fifth or higher principal quantum number ii) when their loss does not afford a species with a noble gas configuration. This property of stabilising the lower oxidation state keeping the paired electron in the ns orbital is referred to as the `inert pair effect'. This effect is also observed in the elements of groups 12 (IIB), 14(IVA) and 15(VA) where the heavier elements exhibit 0, +2 and +3 oxidation states respectively.

Nature of oxides

Oxides of p-block elements may be basic (in case of metallic elements), amphoteric (in case of metalloids) or acidic (in case of non-metals). Non-metals also form a number of oxyacids. In all the groups, the acidic character of the oxide decreases as we move down the group while it increases in the same period from left to right.

For example

Basic oxide - Bi_2O_3

Amphoteric oxide - SnO, SnO_2, PbO, Pb_2O_3

Acidic oxides - SO_3, Cl_2O_7

Oxyacids - HNO_3, H_2SO_4.

Basic character increases down the group

CO_2	SiO_2	GeO_2	SnO	PbO
acidic	less acidic	amphoteric	basic	most basic

Acidic character increases across a period

Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O_7
amphoteric	acidic			most acidic

Nature of hydrides

Many of the p-block elements form hydrides. The hydrides of non-metals are more stable. Thus in any group the stability of the hydride decreases from top to bottom; its strength as an acid also increases in this order. Thus among all the hydrides, hydrogen iodide forms the strongest acid solution in water. In group 15, nitrogen forms the stablest hydride of all. Thus the order of stability of these hydrides is

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Nature of halides

Out of the p-block elements, the non-metals form covalent halides. Metallic halides show a gradation from an ionic character to covalent character. As we move from left to right across the period, ionic character of the halides decreases and covalent character increases. For example, $SbCl_2$ is partially ionic whereas $TeCl_4$ is covalent.

In case metals forms halides in more than one oxidation states, halides in lower oxidation state are largely ionic and those in higher oxidation state are largely covalent.

Polarizability of a halide ion depends on its size. Iodides and bromides are more covalent while fluorides are more ionic.

7.2 Group 13 - Boron Group (B, Al, Ga, In, Tl)

Boron exists in two allotropic forms amorphous and crystalline boron. Boron is a non-metallic element and is a non-conductor of electricity.

Chemical properties

1) **Action of air:-** It is unaffected by air at ordinary temperature but when heated in air to about 975K, it burns forming boron trioxide and a little boron nitride, BN

$$4B + 3O_2 \rightarrow 2B_2O_3$$

$$2B + N_2 \rightarrow 2BN$$

2) **With acids: -** Amorphous boron dissolves in hot concentrated sulphuric and in nitric acid to form boric acid.

$$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO_2$$

$$2B + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3SO_2.$$

3) **With caustic alkali:-** It dissolves in fused caustic alkali and forms boric acid.

4) **As a reducing agent:-** Boron is a powerful reducing agent and can even replace carbon from carbon dioxide and silicon from silica.

$$3CO_2 + 4B \rightarrow 2B_2O_3 + 3C$$

$$3SiO_2 + 4B \rightarrow 2B_2O_3 + 3Si$$

5) **With metals:-** It combines with metals (except Cu, Ag and Au) at high temperature in the electric furnace to form borides.

6) **With non-metals:-** Boron combines with nitrogen, chlorine, bromine and carbon at higher temperature forming boron nitride, BN, boron trichloride, BCl_3, boron tribromide, BBr_3 and boron carbide, B_4C respectively. Boron carbide is probably the hardest substance known.

7.2.3 Compounds of Boron

Borax (or) Sodium tetraborate, $Na_2B_4O_7$ - Tincal, a crude form of borax, contains 55% of it and is found in the land dried up lakes of Tibet.

Borax can be prepared

i) **From colemanite:-** It is boiled with concentrated solution of sodium carbonate.

2. Formation of ozone

Atomic oxygen combines with molecular oxygen to give ozone which may be condensed by means of liquid air

$$O_2 + [O] \longrightarrow O_3$$

3. Oxidation

Atomic oxygen is an extremely powerful oxidizing agent and oxidises aliphatic and aromatic hydrocarbons and methyl alcohol with emission of heat and light. With nitric oxide, a characteristic greenish - white luminescence is produced. H_2S and CS_2 react with it and burst into greyish blue coloured flame.

7.6.2 Oxides

Generally all the elements react with dioxygen to form oxides. Oxides are binary compounds of oxygen. Oxides may be classified depending on their structure (or) their chemical properties.

i) Acidic oxides

The oxides of non-metals are usually covalent and acidic. They have low melting and boiling points, though some B_2O_3 and SiO_2 form infinite "giant molecules" and have high melting points. They are all acidic. Some oxides dissolve in water and thus forming acids. Hence they are called as acid anhydrides

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

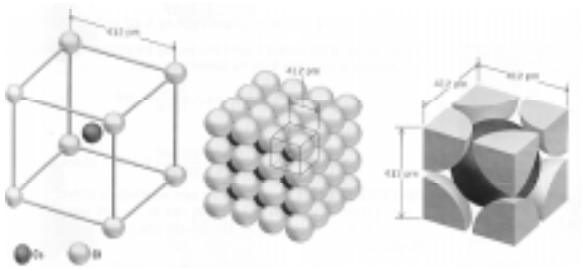
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

others which do not react with water such as SiO_2 reacts with NaOH and shows acidic properties.

ii) Basic oxides

Metallic oxides are generally basic. Most metal oxides are ionic and contain the O^{2-} ion. Some oxides dissolve in water and form alkaline solution.



1. The Cl^- ions are at the corners of a cube where as Cs^+ ion is at the centre of the cube or vice versa
2. Each Cs^+ ion is connected eight Cl^- ions and each Cl^- ion is connected eight Cs^+ ions i.e., 8:8 coordination. Thus each atom is at the center of a cube of atoms of the opposite kind, so that the coordination number is eight.

The unit cell of cesium chloride has one Cs^+ ion and one Cl^- ion as shown below

No. of Cl^- ions

= 8(At corners) x 1/8 (common to eight unit cell)

= 8 x 1/8 = 1

No. of Cs^+ ion = 1 (At the body center) x 1

= 1 x 1 = 1

Thus number of CsCl units per unit cell is 1.

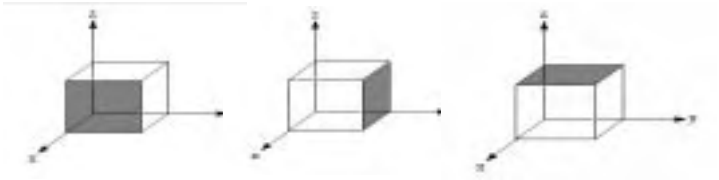
Representative crystals having the CsCl arrangements include: CsBr, CsI, TlBr, TlI, NH_4Cl etc.

8.3 Miller Indices

The geometry of a crystal may be completely defined with the help of coordinate axes all meeting at a point (origin). The number and inclination of these crystal intercept them at definite distances from the origin or are parallel to some of the axes, i.e., intercepting at infinity. The law of rational indices or intercepts states that it is possible to choose along the three coordinate axes unit distances (a, b, c) not necessarily of the same length such that the ratio of the intercepts of any plane in the crystal is given by (la : mb : nc) where l, m and n are simple integers like 1, 2, 3 or fractions of whole numbers.

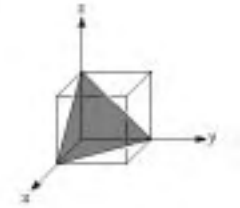
x = ∞, y = 1, z = ∞ because the plane is parallel to the x- and z-axes, forming the Miller indices gives (010). The top plane has intercepts x = ∞, y = ∞ , z = 1 because the plane is parallel to the x- and y- axes , forming the Miller indices gives (001).

The (110) plane intercepts x=1, y=1 and z= ∞ which is parallel to z-axis. Similarly the other two planes are (101) and (011). The (111) plane intercepts all the three axes x=1, y=1 and z=1.



(100) (010) (001)

(110) (101) (011)



(111)

Example 1: Calculate the Miller indices of crystal planes which cut through the crystal axes at (i) (2a, 3b, c) (ii) (a, b, c) (iii) (6a, 3b, 3c) and (iv) (2a, -3b, -3c).

Solution : following the procedure given above, we prepare the tables as follows:

C. Write in one or two sentence :

1. What governs the packing of particles in crystals?
2. What is meant by ‘unit cell’ in crystallography?
3. How many types of cubic unit cell exits?
4. What are Miller Indices?
5. Mention the number of sodium and chloride ions in each unit cell of NaCl
6. Mention the number of cesium and chloride ions in each unit cell of CsCl

D. Explain briefly on the following :

1. Define and explain the following terms
   a) Crystalline solids b) Amorphous solids c) Unit cell
2. Give the distinguishing features of crystalline solids and amorphous solids.
3. Explain the terms Isotropy and Anisotropy.
4. What is the difference between body centred cubic and face centred cubic?
5. Draw a neat diagram for sodium chloride structure and describe it accordingly.
6. Draw a neat diagram for Cesium chloride structure and describe it accordingly.

Problems

1. How many atoms are there per unit cell in (i) simple cubic arrangement of atoms, (ii) body centred cubicarrangement of atoms, and (iii) face-centred cubic arrangement of atoms?
   Ans: (i) : 1, (ii) : 2 and (iii) : 4
2. How do the spacings of the three planes (100), (101) and (111) of simple cubic lattice vary?
   Ans: 1: 1/ √ 2 : 1/ √ 3
3. How do the spacings of the three planes (001), (011) and (111) of bcc lattice vary?
   Ans: 1/2 : 1/ √ 2 : 1/ 2√ 3
4. How do the spacings of the three planes (010), (110) and (111) of fcc lattice vary?
   Ans: 1/2 : 1/ 2√ 2 : 1/ √ 3

SUMMARY

Solids form an important part of the world around us, providing materials with a definite shape and predictable properties.

Crystalline solids are made of ordered arrays of atoms, ions or molecules.

Amorphous solids have no long-range ordering in their structures.

The unit cell is the basic repeating unit of the arrangement of atoms, ions or molecules in a crystalline solid.

Lattice refers to the three dimensional array of particles in a crystalline solid. Each particle occupies a lattice point in the array.

A simple cubic unit cell has lattice points only at the eight corners of a cube.

A body-centred cubic unit cell has lattice points at the eight corners of a cube and at the centre of the cube.

A face-centred cubic unit cell has the same kind of particles (lattice paints) at the eight corners of a cube and at the centre of each face.

The geometry of the crystal may be completely defined with the help of coordinate axes meeting at a point.

The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axes.

The study of crystal is known as crystallography.

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$$P = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V}$$

$$\therefore \quad PV = (n_A + n_B + n_C)\, RT$$

This equation is known as **equation of state of gaseous mixture.**

Calculation of Partial Pressure

In order to calculate the pressure (p_A) of the individual component say A, in a mixture (A and B), which is equal to the partial pressure of A, according to the equation of state of gaseous mixture it is seen that,

P = Total pressure of the mixture

$$P = (n_A + n_B)\frac{RT}{V}$$

$$\text{But } p_A = \frac{n_A}{V} RT \quad \text{and} \quad p_B = \frac{n_B}{V} RT$$

The ratio is given by

$$\frac{p_A}{P} = \frac{p_A}{(n_A + n_B)} \cdot \frac{V}{RT} \cdot \frac{RT}{V}$$

$$= x_A = \text{mole fraction of A.}$$

Or $\boxed{p_A = X_A P}$

i.e:- Partial pressure, p_A = mole fraction of A x total pressure. Similarly;

$$\boxed{p_B = X_B P}$$

Thus, the partial pressure of the individual component in the mixture can be calculated by the product of its mole fraction and total pressure.

Problem 1

Calculate the partial pressures N_2 and H_2 in a mixture of two moles of N_2 and two moles of H_2 at STP.

decrease the volume. This effect makes liquefaction to commence at higher pressure compared to the previous isotherm at 13.1°C.

At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1°C it reduces to a point. The temperature 31.1°C is regarded as the critical temperature of CO_2. At this temperature, the gas passes into liquid imperceptibly. Above 31.1°C the isotherm is continuous. CO_2 cannot be liquefied above 31.1°C no matter how high the pressure may be. The portion of area covered by curve H with zyx portion always represents the gaseous state of CO_2.

9.8.2 Continuity of state

Thomson's experiment

Thomson (1871) studied the isotherm of CO_2 drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. Thus, he showed a theoretical wavy curve. The curve MLPin Fig.9.7 represents a gas compressed in a way that it would remain stable. The curve LMNC represents a superheated liquid because compression above T_c leads to heating effects. This type of continuity of state is predicted by Vanderwaal's equation of state which is algebraically a cubic equation. The Vanderwaal's equation may be written as

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

expanding the expression,

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying by V^2

$$PV^3 - (RT + Pb)V^2 + aV - ab = 0$$

Solution

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

$$= \frac{8 \times 3.67}{27 \times 0.0821 \times 0.0408} = 324.7 \text{ K}$$

$$= 51.7^{\circ}C$$

$$P_c = \frac{a}{27b^2} = \frac{3.67}{27 \times (0.0408)^2}$$

$$= 81.6 \text{ atm}$$

Problem 6

The critical temperature of hydrogen gas is 33.2°C and its critical pressure is 12.4 atm. Find out the values of 'a' and 'b' for the gas.

Solution: We know

$$T_c = \frac{8a}{27Rb} \quad \text{... (i)}; \qquad P_c = \frac{a}{27b^2} \quad \text{.... (ii)}$$

Dividing (i) by (ii) we get

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R} \quad \text{...(iii)}$$

Given $T_c = 33.2^{\circ}C = 33.2 + 273 = 306.2K$ and $P_c = 12.4$ atm; $R = 0.082$ atm. litre $K^{-1}mol^{-1}$. Substituting the values in equation (iii), we get

$$\frac{306.2}{12.4} = \frac{8 \times b}{0.082}$$