

1

STOICHIOMETRY



After completing this lesson, you will be able to:

**This is 10 days lesson
(period including homework)**

- Understand the Given information from which any two of the following may be determined, calculate the theoretical yield, actual yield and percentage yield.
- Interpret a balanced chemical equation in terms of interacting moles, representative particles, masses and volumes of gases at STP.
- Perform stoichiometric calculations with balanced equation using moles, representative particles, masses and volumes of gases (at STP).
- Know the limiting reagent in a reaction, calculate the maximum amount of product (s) produced and the amount of any unreacted excess reagent.
- Construct mole ratios from balanced equations for use as conversion factors in stoichiometric problems.
- Calculate the theoretical yield and the percent yield from the given balanced equation, the amounts of the reactants and the actual yield.

INTRODUCTION

It is observed that a common factor for fireworks manufacturer, an engineer to design car engines and a chemist to manufacture a chemical plant is the amount of materials they need in their specific area of work.

For examples,

1. Fireworks manufacturer is required to mix calculated amounts of chemicals. A wrong calculated amount could result in violent explosions.
2. The engineer must know the relative amounts of fuel and oxygen needed for efficient combustion.
3. A chemist is required to use calculated amounts of reactants to produce exact amount of products.

Such phenomenon is studied through the knowledge of Stoichiometry (Greek words Stoichein means element and metry means measurement). **The study of relative amounts of substances involved in a chemical reaction is called Stoichiometry. The amounts of reactants and products in a balanced chemical equation are called Stoichiometric Amounts.** Such study is essential when quantitative information about a chemical reaction is required. Moreover it is important to predict yields of chemical products.

1.1 MOLE

The atomic mass, formula mass and molecular mass of a substance expressed in grams is called Mole.

Examples

One mole of O (atom) = 16 g

One mole of O₂ (molecule) = 32 g

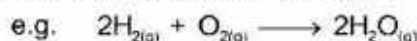
One mole of H₂O (molecule) = 18 g

One mole of Na⁺ (ion) = 23 g

One mole of NaCl (Formula unit) = 58.5 g

1.2 AVOGADRO'S NUMBER

"The number of atoms, ions or molecules present in one mole of a substance is called Avogadro's Number". Its numerical value is 6.023×10^{23} . One mole of any gas at S.T.P occupies 22.414 dm³ and contains 6.02×10^{23} particles.



This reaction can also be expressed in terms of Avogadro's number. The equation states that $2 \times 6.02 \times 10^{23}$ molecules of hydrogen react with 6.02×10^{23} molecules of oxygen to produce $2 \times 6.02 \times 10^{23}$ molecules of water.

The relationship between moles and Avogadro's number in different substances is as follows:

1 mole of O-atoms = 6.02×10^{23} atoms

1 mole of O_{2(g)} = 6.02×10^{23} molecules

1 mole of H₂O_(l) = 6.02×10^{23} molecules

1 mole of NaCl_(s) = 6.02×10^{23} formula units

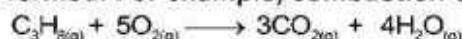
In the case of ionic compounds, the explanation is somewhat different.

For example, $\text{NaCl} \xrightarrow{\text{H}_2\text{O}} \text{Na}_{(aq)}^{+1} + \text{Cl}_{(aq)}^{-1}$

It shows that 1 mole of NaCl when dissolves in water gives 1 mole of Na¹⁺ ions and 1 mole of Cl⁻¹ ions. So According to Avogadro's number we can say that when 6.02×10^{23} formula units of NaCl are dissolved in water, they produce 6.02×10^{23} Na¹⁺ and 6.02×10^{23} Cl⁻¹ ions.

Mole Ratios

Mole ratio means the ratio of no. of moles of reactants taking part and the no. of moles of products formed. For example, combustion of propane



The mole ratios between the reactants and products can be shown as, one mole of C₃H₈ reacts with five moles of oxygen to give three moles of CO₂ and four moles of water. The amount of propane used will not affect these ratios.

Example 1.1

Methanol burns according to the following equation.



If 3.50 moles of methanol are burnt in oxygen, calculate

- (a) How many moles of oxygen are used?
 (b) How many moles of water are produced?

Solution

- (a) Moles of methanol = 3.50 moles
 Moles of oxygen = ?

According to balanced chemical equation



$$3.5 \text{ moles of CH}_3\text{OH} = \frac{3.50 \times 3}{2} \text{ moles of O}_2$$

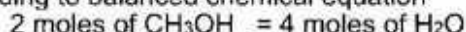
$$= 5.25 \text{ moles of O}_2$$

So the number of moles of O_2 consumed = 5.25 moles

- (b) No. of Moles of CH_3OH = 3.5 moles

No. of Moles of H_2O = ?

According to balanced chemical equation



$$3.5 \text{ moles of CH}_3\text{OH} = \frac{3.50 \times 4}{2} \text{ moles of H}_2\text{O}$$

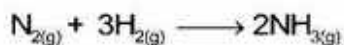
$$= 7.00 \text{ moles of H}_2\text{O}$$

So the number of moles of H_2O produced = 7.00 moles



Self Check Exercise 1.1

NH_3 is an important raw material in the manufacture of fertilizers. It is obtained by the combination of N_2 and H_2 as shown by the following balanced equation.



How many moles of the following are required to manufacture 5.0 moles of NH_3 ?

- (a) Nitrogen (b) Hydrogen

(Ans: (a) N_2 = 2.5 moles (b) H_2 = 7.5 moles)

Example 1.2

Iron can be produced from iron ore Fe_2O_3 by reacting the ore with carbon monoxide (CO). Carbon dioxide (CO_2) is produced in this reaction as a by product. What mass of iron can be formed from 425 g of iron ore?



1. Stoichiometry

9

Solution

The balanced equation can be written as



Mass of iron ore = 425 g (given mass)

$$\begin{aligned}\text{No of moles of iron ore} &= \frac{\text{mass}}{\text{molecular mass}} = \frac{425 \text{ g}}{159.6 \text{ g moles}^{-1}} \\ &= 2.66 \text{ moles of Fe}_2\text{O}_3\end{aligned}$$

According to balanced chemical equation

1 mole of Fe_2O_3 = 2 moles of Fe

2.66 moles of Fe_2O_3 = 2.66×2 Moles of Fe = 5.32 Moles of Fe

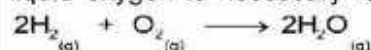
Mass of Fe produced = no. of moles of Fe $\times$ Molar mass of iron
= $5.32 \times 55.9 \text{ g}$

Mass of iron produced = 297.388 g



Self Check Exercise 1.2

The main engines of the U.S. space shuttle are powered by liquid hydrogen and liquid oxygen. If $1.02 \times 10^5 \text{ kg}$ of liquid hydrogen is carried on a particular launch, what mass of liquid oxygen is necessary for all the hydrogen to burn. The equation for the reaction is,



(Ans: $8.16 \times 10^5 \text{ kg}$ oxygen)

Example 1.3

Calculate the no of molecule of O_2 produced by thermal decomposition of 490 grams of KClO_3

Solution:

The given mass of KClO_3 = 490 g

Formula mass of KClO_3 = $122.5 \text{ g mole}^{-1}$

No. of moles of KClO_3 = $490 / 122.5$
= 4 moles

According to reaction, $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$

2 moles of KClO_3 = 3 moles of O_2

4 moles of KClO_3 = $3/2 \times 4$

= 6 moles of O_2

1 mole of O_2 = 6.02×10^{23} molecules of O_2

6 moles of O_2 = $6 \times 6.02 \times 10^{23}$ molecules of O_2

= 3.612×10^{24} molecules of O_2

Example 1.4

20g of H_2SO_4 on dissolving in water ionizes completely. Calculate

- No of H_2SO_4 molecules
- No of H^+ and SO_4^{2-}
- Mass of individual ion

Solution

$$\begin{aligned}
 \text{a. Mass of H}_2\text{SO}_4 &= 20\text{g} \\
 \text{Molar Mass of H}_2\text{SO}_4 &= 98.016\text{g mole}^{-1} \\
 \text{No of molecules of H}_2\text{SO}_4 &= \frac{\text{Mass of H}_2\text{SO}_4}{\text{Molar Mass of H}_2\text{SO}_4} \times 6.02 \times 10^{23} \\
 &= \frac{20}{98.016} \times 6.02 \times 10^{23} \\
 &= 1.228 \times 10^{23}
 \end{aligned}$$

b. H_2SO_4 dissolves in water as follows:



According to equation

$$1 \text{ molecule of H}_2\text{SO}_4 = 2\text{H}^+ \text{ ions}$$

$$\begin{aligned}
 1.228 \times 10^{23} \text{ molecules of H}_2\text{SO}_4 &= 2 \times 1.228 \times 10^{23} \text{ H}^+ \text{ ions} \\
 &= 2.456 \times 10^{23} \text{ H}^+ \text{ ions}
 \end{aligned}$$

$$\text{As } 1 \text{ molecule of H}_2\text{SO}_4 = 1 \text{ SO}_4^{2-} \text{ ions}$$

$$\text{So, } 1.228 \times 10^{23} \text{ molecule of H}_2\text{SO}_4 = 1.228 \times 10^{23} \text{ SO}_4^{2-} \text{ ions}$$

$$\begin{aligned}
 \text{c. Mass of individual ions} &= \frac{\text{No. of ions}}{6.02 \times 10^{23}} \times \text{Molar mass of an ion} \\
 \text{Mass of H}^+ &= \frac{2.456 \times 10^{23}}{6.02 \times 10^{23}} \times 1.008 \\
 &= 0.411\text{g} \\
 \text{Mass of SO}_4^{2-} &= \frac{1.228 \times 10^{23}}{6.02 \times 10^{23}} \times 96 \\
 &= 19.58\text{g}
 \end{aligned}$$

Molar Volume

One mole of any gas at STP (standard temperature and pressure) occupies a volume of 22.414 dm^3 . This volume is called **Molar volume**. With the help of this relationship, we can convert the mass of a gas at STP into its volume and vice versa. Hence we can say molar volume of gases is also related with their density at STP (see section 4.4.3).

$$22.414 \text{ dm}^3 \text{ of any gas at STP} = 1 \text{ mole} = 6.02 \times 10^{23} \text{ molecules.}$$

$$22.414 \text{ dm}^3 \text{ of H}_2 \text{ gas at STP} = 2\text{g} = 6.02 \times 10^{23} \text{ molecules.}$$

$$22.414 \text{ dm}^3 \text{ of NH}_3 \text{ gas at STP} = 17\text{g} = 6.02 \times 10^{23} \text{ molecules.}$$

Example 1.5

Determine the volume that 2.5 moles of chlorine molecules occupy at STP.

Solution:

We know that

$$22.414 \text{ dm}^3 \text{ of Cl}_2 \text{ (Chlorine) at STP} = 1 \text{ mole}$$

$$\text{or } 1 \text{ mole of Cl}_2 \text{ occupies a volume of } 22.414 \text{ dm}^3 \text{ at STP.}$$

$$2.5 \text{ mole of Cl}_2 \text{ occupy a volume of } 22.414 \text{ dm}^3 \times 2.5 = 56.035 \text{ dm}^3$$

**Self Check Exercise 1.3**

- (a) How many moles of oxygen molecule are there in 50.0 dm³ of oxygen gas at S.T.P?
- (b) What volume does 0.80 mole of N₂ gas occupy at S.T.P?

(Ans: (a) 2.23 moles, (b) 17.93 dm³)

1.3 PERCENTAGE COMPOSITION

The relative amounts of each element in a compound are expressed as the percentage composition. For example the percentage composition by mass in MgO is as follows,

To determine the percentage composition of a known compound,

- I) Calculate the molar mass of compound
- II) Calculate the percentage of each element in one mole of the compound. This is done by dividing the mass of each element in one mole of the compound by the molar mass multiplied by 100.

$$\% \text{ of an element} = \frac{\text{mass of element in 1 mole of compound}}{\text{molar mass of compound}} \times 100$$

1.4 LIMITING AND NON LIMITING REACTANTS

The reactant that is consumed completely in a chemical reaction is called limiting reactant. Also it can be defined as the reactant which produces the least number of moles of products in a chemical reaction. The reactant left un-used or un-reacted after completion of reaction is called Reactant in excess or Non Limiting reactant.

A limiting reactant can be recognized by calculating the number of moles of products formed from data of the given amounts of the reactants, using a balanced chemical equation. The reactant, which produces the least number of moles of products, is the limiting reactant.

For example, 10 moles of H₂ and 7 moles of O₂ were reacted to produce H₂O. Which one of the reactant is the limiting reactant? We can calculate as follows:



Stoichiometrically,

According to balanced chemical equation

- (i) — $2\text{H}_2 = 2\text{H}_2\text{O}$
 i.e. 2 moles of H₂ = 2 moles of H₂O
 $10 \text{ moles of H}_2 = \frac{2}{2} \times 10 = 10 \text{ moles of H}_2\text{O}$
- (ii) $\text{O}_2 = 2\text{H}_2\text{O}$
 i.e. 1 mole of O₂ = 2 moles of H₂O
 so, 7 moles of O₂ = $2 \times 7 = 14 \text{ moles of H}_2\text{O}$

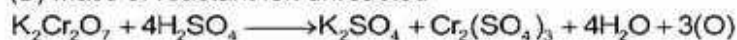
Since H₂ gives the least number of moles of H₂O, i.e. 10 moles, so H₂ is the limiting reactant.

Example 1.6

200 g of $K_2Cr_2O_7$ were reacted with 200g conc. H_2SO_4 . Calculate

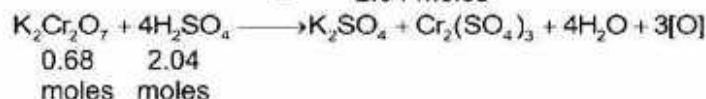
(A) Mass of atomic oxygen produced

(B) Mass of reactant left unreacted



Solution:

$$\begin{aligned}
 \text{(a) Mass of } K_2Cr_2O_7 &= 200\text{g} \\
 \text{Formula Mass of } K_2Cr_2O_7 &= 294\text{g mole}^{-1} \\
 \text{No of moles of } K_2Cr_2O_7 &= \frac{200}{294} \\
 &= 0.68 \text{ moles} \\
 \text{Mass of } H_2SO_4 &= 200\text{g mole}^{-1} \\
 \text{Formula Mass of } H_2SO_4 &= 98\text{g mole}^{-1} \\
 \text{No of moles of } H_2SO_4 &= \frac{200}{98} \\
 &= 2.04 \text{ moles}
 \end{aligned}$$



According to balanced chemical equation

$$\begin{aligned}
 1 \text{ mole of } K_2Cr_2O_7 &= 3 \text{ moles of } [O] \\
 0.68 \text{ mole of } K_2Cr_2O_7 &= 3 \times 0.68 \text{ moles of } [O] \\
 &= 2.04 \text{ moles of } [O] \\
 4 \text{ moles of } H_2SO_4 &= 3 \text{ moles of } [O] \\
 2.04 \text{ moles of } H_2SO_4 &= \frac{3}{4} \times 2.04 \\
 &= 1.53 \text{ moles}
 \end{aligned}$$

As H_2SO_4 is producing lesser moles of product so, H_2SO_4 is the limiting reactant.

$$\begin{aligned}
 \text{Mass of atomic oxygen is} &= \text{No. of moles of oxygen atom} \times \text{atomic mass} \\
 &= 1.53 \times 16 = 24.4 \text{ g}
 \end{aligned}$$

b) In this problem H_2SO_4 is the limiting reactant and $K_2Cr_2O_7$ is the reactant in the excess

We have 0.68 moles of $K_2Cr_2O_7$ and 2.04 moles of H_2SO_4

According to the reaction,

$$\begin{aligned}
 4 \text{ moles of } H_2SO_4 &= 1 \text{ mole of } K_2Cr_2O_7 \\
 2.04 \text{ moles of } H_2SO_4 &= \frac{1}{4} \times 2.04 \\
 &= 0.51 \text{ moles of } K_2Cr_2O_7
 \end{aligned}$$

$$\text{No of moles of } K_2Cr_2O_7 \text{ left unreacted} = 0.68 - 0.51$$

$$= 0.17 \text{ moles}$$

$$\text{Mass of } K_2Cr_2O_7 = \text{No of moles} \times \text{Formula Mass of } K_2Cr_2O_7$$

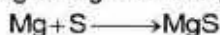
$$= 0.17 \times 294 = 49.98$$

$$\text{So Mass of } K_2Cr_2O_7 \text{ left unreacted} = 49.98\text{g}$$



Example 1.7

Magnesium metal reacts with Sulphur to produce MgS. How many grams of magnesium sulphide (MgS) can be made from 1.50g of Mg and 1.50g of sulphur by the reaction?



Solution:

Mass of Mg	= 1.50g
No. of moles of Mg	$= \frac{1.50}{24} = 0.0625 \text{ moles}$
Mass of S	= 1.50g
No. of moles of S	$= \frac{1.50}{32} = 0.0468 \text{ moles}$



i.e. 1 mole of Mg	= 1 mole of MgS
so, 0.0625 moles of Mg	= 0.0625 moles of MgS
also, 1 mole of S	= 1 mole of MgS
so, 0.0468 moles of S	= 0.0468 Moles of MgS

Since S gives the least No of moles of products as compared to Mg, so it is the limiting reactant.

Now we calculate the mass of MgS in grams.

Mass of 1 Mole of MgS	= 24+32	= 56g
Mass of 0.0468 Mole of MgS	= 56 x 0.0468g	= 2.620g



Self Check Exercise 1.4

- (1) Zinc and Sulphur react to form Zinc Sulphide according to the following balanced chemical equation $\text{Zn} + \text{S} \longrightarrow \text{ZnS}$

If 6.00g of Zinc and 4.00g of Sulphur are available for reaction, then determine

- (a) The limiting reactant.
(b) The mass of Zinc Sulphide produced.

(Ans. (a) Zinc is the limiting reactant since the whole is consumed.

(b) Mass of Zinc Sulphide produced = 8.95g)

- (2) Aluminium reacts with bromine to form Aluminium bromide, as shown by the balanced chemical equation, $2\text{Al} + 3\text{Br}_2 \longrightarrow 2\text{AlBr}_3$

If 15.8g of Al and 55.6g of Br_2 are available for reaction, then determine

- (a) The limiting reactant (b) The mass of AlBr_3 produced

(Ans: (a) Bromine is the limiting reactant. (b) Mass of AlBr_3 formed = 61.9g

During a reaction in which two reactants are reacted sometimes one component is consumed completely and some amount of other reactant is left unreacted. The reactant which is consumed completely during the reaction is called Limiting Reactant and the reactant whose some amount is left unconsumed is called "Reactant in Excess".

The concept of reactant in excess may be more clear by studying the following sample problem.

Example 1.8

Suppose 1.87 moles of ammonium chloride were reacted with 1.35 mole of calcium hydroxide. How many grams of calcium hydroxide are left unreacted in this reaction?

Solution: According to the reaction,



Let us calculate the no. of moles of Ca(OH)_2 in above example that reacts completely with 1.87 moles of NH_4Cl .

$$2 \text{ moles of } \text{NH}_4\text{Cl} = 1 \text{ mole of } \text{Ca(OH)}_2$$

$$1.87 \text{ moles of } \text{NH}_4\text{Cl} = \frac{1}{2} \times 1.87$$

$$= 0.935 \text{ moles of } \text{Ca(OH)}_2$$

$$\text{So, no. of moles of } \text{Ca(OH)}_2 \text{ consumed} = 0.935 \text{ moles}$$

$$\text{And no. of moles of } \text{Ca(OH)}_2 \text{ initially present} = 1.35 \text{ moles}$$

$$\text{So, no. of moles of } \text{Ca(OH)}_2 \text{ unreacted} = 1.35 - 0.935$$

$$= 0.415 \text{ moles}$$

$$\text{Molar mass of } \text{Ca(OH)}_2 = 74$$

$$\text{Mass of } \text{Ca(OH)}_2 = \text{No. of moles} \times \text{Molar mass}$$

$$\text{Mass of } \text{Ca(OH)}_2 = 0.415 \times 74$$

$$= 30.71\text{g}$$

Result: The excess amount of Ca(OH)_2 , which is left unreacted is 30.71g.

1.5 THEORETICAL YIELD, ACTUAL YIELD AND PERCENT YIELD

"The quantity of a product calculated from a balanced chemical equation is called theoretical yield of the reaction". The quantity of a product that is actually produced in a chemical reaction is called the actual yield.

The percent yield can be calculated as,

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

There are many reactions for which the actual yield is almost equal to the theoretical yield. Such reactions are quantitative, i.e., they can be used in chemical analysis. On the other hand, for some reactions, particularly those involving organic compounds, the actual yield of a reaction is less than the theoretical yield and percent yield, less than 100 %.

The actual yield may be less than the theoretical yield due to following reasons,

- Side reactions may produce by-products
- Some reactions are reversible
- Mechanical loss takes place due to filtration, distillation, and separation by separating funnel, washing and crystallization etc.

Example 1.9

In an industry Copper metal was prepared by the following reaction,





1.274g CuSO_4 when reacted with excess of Zn metal a yield of 0.392g of Cu metal is obtained. Calculate the percentage yield.

Solution:

Mass of CuSO_4 given = 1.274g

Now we convert the no of grams of CuSO_4 into no. of moles.

Molecular mass of CuSO_4 = $63.5 + 32 + 64 = 159.5$ g/mole

159.5g of CuSO_4 = 1 mole

1.274 g of CuSO_4 = $\frac{1}{159.5} \times 1.274$
= 7.982×10^{-3} moles.

Stoichiometrically

1 mole of CuSO_4 = 1 mole of Cu

7.98×10^{-3} moles of CuSO_4 = 7.982×10^{-3} moles of Cu.

as, 1 mole of Cu = 63.5 g

so, 7.982×10^{-3} moles of Cu = $63.5 \times 7.982 \times 10^{-3}$
= 0.5072 g of Cu.

Hence, Theoretical yield = 0.5072 g

Actual yield = 0.392 g

So, % yield = $\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$
= $\frac{0.392}{0.5072} \times 100 = 77.3\%$

Example 1.10

In a reaction, 2.00 moles of CH_4 were reacted with an excess of Cl_2 . As a result, 177.0 g of CCl_4 is obtained. What is the

(a) theoretical yield (b) actual yield (c) % yield of this reaction?

Solution:

Reaction is, $\text{CH}_{4(g)} + 4\text{Cl}_{2(g)} \longrightarrow \text{CCl}_{4(l)} + 4\text{HCl}_{(g)}$

Stoichiometrically,

From 2.0 moles of CH_4 , we would expected to obtained 2.0 moles of CCl_4

(a) Theoretical yield = 2.0 moles of CCl_4

Mass of CCl_4 = No. of moles x molar mass

= $2 \times 154 = 308\text{g}$

(b) Actual yield = 177.0g of CCl_4

(c) Percent Yield:

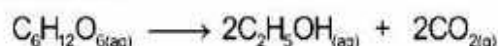
% yield = $\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$

% yield = $\frac{177}{308} \times 100$

= 57.46 %

**Self Check Exercise 1.5**

1. The overall balanced equation for the production of ethanol ($\text{C}_2\text{H}_5\text{OH}$) from glucose is as follows:



- (a) What is the theoretical yield of ethanol available from 10.0 g of glucose?
 (b) If in a particular experiment, 10.0 g of glucose produces 0.664 g of ethanol, what is the percentage yield?

(Ans: (a) Theoretical yield of ethanol = 5.152g (b) Percentage yield = 12.89 %)

2. Solid carbon dioxide (dry ice) may be used for refrigeration. Some of this carbon dioxide is obtained as a by-product when hydrogen is produced from methane in the following reaction.

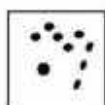


- (a) What mass of CO_2 should be obtained from 1250 g of methane?
 (b) If the actual yield obtained is 3000 g then what is the percentage yield?

(Ans: a = 3437.5 g b = 87.3 %)

References for additional information

- James Brady and John R. Holum, Chemistry, The studies of matter and its changes.
- Theodore L. Brown, H. Eugene LeMay Jr and Bruce E. Bursten, Chemistry, The central Science.
- Rose Marie Gallagher and Paul Ingram, Complete chemistry.
- Graham Hill and John Holman, Chemistry in Context
- E. N. Ramesden, Calculations for A-Level chemistry.



1. Select the most suitable answer in the following MCQs.

- i. How many molecules are there in one mole of H_2O ?
- | | |
|----------------------------|----------------------------|
| (a) 6.023×10^{19} | (b) 6.023×10^{23} |
| (c) 1.084×10^{18} | (d) none of these |
- ii. A flask contains 500 cm^3 of SO_2 at STP. The flask contains;
- | | |
|----------|------------|
| (a) 40 g | (b) 100 g |
| (c) 50 g | (d) 1.427g |



- iii. A necklace has 6g of diamond in it. What are the numbers of atoms in it?
(a) 6.02×10^{23} (b) 12.04×10^{23}
(c) 1.003×10^{23} (d) 3.01×10^{23}
- iv. What is the mass of aluminium in 204 g of the aluminium oxide, Al_2O_3 ?
(a) 26 g (b) 27 g
(c) 54 g (d) 108 g
- v. The reactant which is consumed earlier and gives least quantity of product is called;
(a) Reactant in excess (b) Stoichiometry
(c) Limiting reactant (d) Stoichiometric amount
- vi. Which one of the following compounds contains the highest percentage by mass of nitrogen?
(a) NH_3 (b) N_2H_4
(c) NO (d) NH_4OH
- vii. Vitamin-A has a molecular formula $\text{C}_{20}\text{H}_{30}\text{O}$. The number of vitamin-A molecules in 500 mg of its capsule will be;
(a) 6.02×10^{23} (b) 1.05×10^{21}
(c) 3.01×10^{22} (d) 3.01×10^{23}
- viii. When one mole of each of the following is completely burnt in oxygen, which will give the largest mass of CO_2 ?
(a) Carbon monoxide (b) Diamond
(c) Ethane (d) Methane
- ix. One mole of ethanol and one mole of ethane have an equal;
(a) Mass (b) Number of Atoms
(c) Number of electron (d) Number of molecules
- x. Methane reacts with steam to form H_2 and CO as shown below,
$$\text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)} \longrightarrow \text{CO}_{(g)} + 3\text{H}_{2(g)}$$

What volume of H_2 can be obtained from 100 cm^3 of methane at the standard temperature and pressure?
(a) 300 cm^3 (b) 200 cm^3
(c) 150 cm^3 (d) 100 cm^3
- xi. The Avogadro's constant is the number of
(a) Atoms in 1g of Helium (b) Molecules in 35.5g of Chloride
(c) Electrons needed to deposit 24g of Mg
(d) Atoms in 24g of Mg
- xii. How many moles of oxygen are needed for the complete combustion of two moles of butane?
(a) 2 (b) 8 (c) 10 (d) 13
- xiii. If four moles of SO_2 are oxidised to SO_3 , how many moles of oxygen molecules are required?
(a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0

- xiv. The relative atomic mass of chlorine is 35.5. What is the mass of 2 moles of Chlorine gas?
 (a) 142g (b) 71g (c) 35.5g (d) 18.75g
- xv. Which of the following statements is incorrect?
 (a) 12g of carbon gas contains one mole of atoms
 (b) 28g of nitrogen gas contains one mole of molecules of N_2
 (c) 1 dm³ of a 1.0 mole dm⁻³ solution of NaCl contains one mole of Chloride ions
 (d) None of above
- xvi. One mole of propane has the same;
 (a) Number of H-atoms as one mole of methane (CH_4)
 (b) Number of C-atoms as in one mole of butane (C_4H_{10})
 (c) Mass as half a mole of hexane (C_6H_{14})
 (d) Number of molecules as in one mole of ethane (C_2H_6)
- xvii. What is the mass of one mole of Iodine Molecules?
 (a) 254 g (b) 74 g (c) 106 g (d) 127 g
- xviii. What volume of SO_2 at room temperature and pressure is produced on heating 9.7g of Zinc Sulphide (ZnS) if reaction takes place as follows:
- $$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$
- (a) 1.2 dm³ (b) 2.4 dm³
 (c) 3.6 dm³ (d) 4.8 dm³

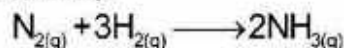
2. Answer the following questions briefly:

- 58.5 amu are termed as formula mass and not molecular mass of NaCl. Why?
- Concept of limiting reactant is not applicable to the reversible reactions. Explain.
- How many covalent bonds are present in 9g of H_2O ?
- Differentiate between limiting and non-limiting reactants.
- How many molecules of water are there in 12 g of ice?
- Which contains more atoms, 1 mole of Fe or 1 mole of H_2 ? Justify your stand.
- Give reason that 1 mole of different compounds have different masses but have the same number of molecules.
- 23g of sodium and 238g of uranium have equal number of atoms in them.
- Calculate the weight of oxygen gas evolved when 5.0 g of $KClO_3$ are completely decomposed thermally.
- What is the relationship between mass and volume of a gas at S.T.P?
- The actual yield is lesser than the theoretical yield. Give reasons?
- What are the representative particles in one mole of a gas at S.T.P?
- What is Stoichiometry and Stoichiometric amounts?

3. (a) What is Avogadro's number? Give examples. How will you explain moles with the help of Avogadro's Number?
- (b) The liquid $CHBr_3$ has a density of 2.89 g cm⁻³. What volume of this liquid should be measured to contain a total of 4.8×10^{24} molecules of $CHBr_3$. (Ans: 696.8 cm³)



4. (a) Differentiate between actual yield and theoretical yield.
(b) The following reaction never goes to completion. Therefore less amount of NH_3 is obtained than expected theoretically,



42.0 g of H_2 produces 120.2 g of NH_3 . Calculate the percentage yield of NH_3 .

(Ans: 50.5 %)

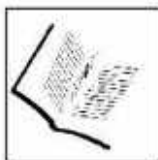
5. (a) What do you know about percentage composition? How will you determine the percentage of each element in the substance?
(b) Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is the most important nutrient in the cell for generating chemical potential energy. Calculate the mass percentage of each element in glucose.
(Ans: C = 40 %, H = 6.66 %, O = 53.33 %)
6. (a) How will you calculate the theoretical yield and percentage yield in a balanced chemical equation?
(b) A small piece of pure Al Metal having a volume of 2.50 cm^3 is reacted with excess of HCl. What is the weight of H_2 liberated? The density of Al is 2.70 g cm^{-3} .

(Ans: 0.752g)

7. How much Silver Chloride will be formed by mixing 120.0 g of Silver Nitrate with a solution of 52.0 g of NaCl?



(Ans: 101.24 g)



2

ATOMIC STRUCTURE



After completing this lesson, you will be able to:

**This is 10 days lesson
(period including homework)**

- Define proton as a unit of radiation energy.
- Use the Bohr's model for calculating the radii of orbits.
- Explain production, properties, types and uses of X-rays.
- Describe the concept of orbitals.
- Distinguish among principal energy levels, energy sub levels, and atomic orbitals.
- Describe the general shapes of s, p and d orbitals.
- Describe the hydrogen atom using the Quantum Theory.
- Describe the orbitals of hydrogen atom in order of increasing energy. Summarize the Bohr's atomic theory.
- Use the Bohr's model for calculating energy of electron in a given orbit of hydrogen atom.
- Relate energy equation (for electron) to frequency, wave length and wave number of radiation emitted or absorbed by electron.
- Explain the significance of quantized energies of electrons.
- Relate the discrete-line spectrum of hydrogen to energy levels of electrons in the hydrogen atom.
- Use the Aufbau Principle, the Pauli Exclusion Principle, and Hund's Rule to write the electronic configuration of the elements. Explain the sequence of filling of electrons in many electron atoms.
- Write electron configuration of atoms.

INTRODUCTION

A series of discoveries beginning during the later part of 19th century have modified the Daltonian concept of the atom by demonstrating that an atom is a complex unit made up of similar discrete parts. Atoms are not simple, compact bodies as supposed by Dalton but are complex systems composed of several fundamental particles of matter. The modern theories have proved that an atom is made up of about 100 particles out of which electrons, protons and neutrons are whole time existing and important particles.

We need to understand atomic structure in order to understand chemical bonds that hold atoms together and chemical reactions.

The atoms are made up of sub-atomic particles, electron, proton and neutron. These three particles are called elementary or fundamental particles as they are building blocks of all atoms. Many of the characteristics of an atom are dependent upon these three particles. The only atom which do not contain neutron is protium (hydrogen). Many other particles such as neutrino, antineutrino, positron, pions and muons have also been discovered. Many of them are unstable and exist for a fraction of second only.

2.1 DISCHARGE TUBE EXPERIMENTS

A gas discharge tube is fitted with two metallic electrodes, as cathode and anode. The tube is filled with a gas, air or vapour of a substance at any desired pressure. The electrodes are connected to a source of high voltage battery. The tube is attached to the vacuum pump as shown in the diagram (2.1). In the beginning an electric current was passed through the gas in the discharge tube at ordinary pressure. The gas in the tube was not affected even at high potential of 5000 volts. However, the gas was discharged from tube up to a low pressure of 0.01 torr, and was connected to high voltage of 5000-10,000 volts. It was observed that at very low pressure of 0.1 torr and high potential, the gas becomes conductor, current starts to flow through the gas and gas starts to emit light (modern example of such a discharge tube is "a neon sign"). When the pressure is reduced

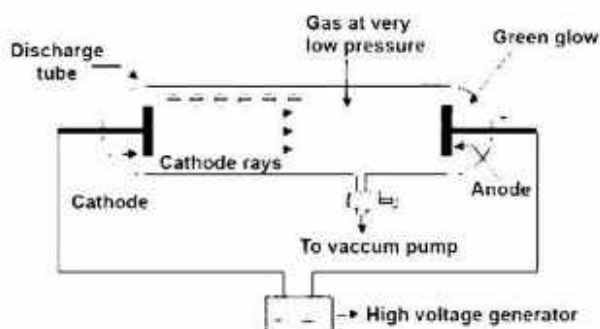


Fig. 2.1: A discharge tube

even further upto 0.01 torr, emission of light by the gas ceased, certain rays were given out from cathode and travel towards anode. Such rays were called cathode rays because they originate from cathode. J.J. Thomson first identified the electrons in cathode ray tube (electric discharge tube) in 1887. Many other scientists like Faraday & Crookes studied the effects of passing electric current through a gas. As a result a sub-atomic particle with a negative charge was discovered.

Through different discharge tube experiments electrons were discovered by J. J. Thomson in 1887 (but the name electrons was given by Stoney in 1886).

Properties of Cathode Rays

Some systematic studies were made by certain scientists in order to investigate the properties of cathode rays. These properties are mentioned below.

Cathode rays are negatively charged particles. J-Perrin (1895) showed that cathode rays are deflected in a magnetic field. J.J. Thomson (1897) proved that these rays can be deflected towards anode showing that they are negatively charged. They produce a greenish fluorescence on striking the walls of the glass tube.

Hittorf (1869) proved that cathode rays cast a sharp shadow when an opaque object is placed in their path. This proves that they travel in straight line perpendicular to the surface of cathode.

They can drive a small paddle wheel placed in their path. This verifies that they are material particles and have certain momentum also.

They can produce X-rays when they strike on an anode, particularly with large atomic mass. They produce

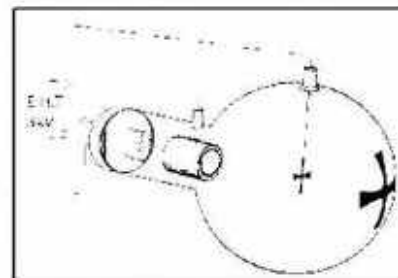


Fig. 2.2: Cathode rays casting shadow of an opaque object

heat when they fall on a platinum foil and foil begins to glow. They can ionize gases. They can cause a chemical change in a material on which they fall. They are capable of penetration in metallic sheets like of Aluminium or Gold.

J.J. Thomson determined charge to mass ratio (e/m) of an electron. He concluded that all atoms contain electrons. The value of e/m is 1.7588×10^{11} Coulombs kg^{-1} . Whatever the gases and the vapour in the discharge tube, the cathode rays and the electrons are always the same. This proves that electrons are present in all atoms.

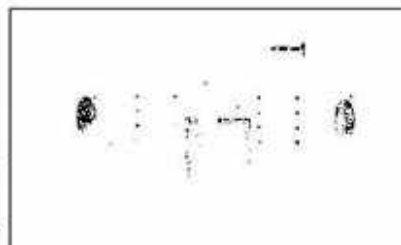


Fig. 2.3: Cathode rays moving a small paddle wheel

Measurement of charge to mass ratio (e/m) and charge of an electron:

(J. J. Thomson's cathode rays experiment 1897)

J. J. Thomson subjected a beam of cathode rays (electron particles) to see the effects of electric and magnetic fields as shown in figure 2.4.

In the beginning, in absence of any electric or magnetic field, the electrons from cathode rays struck the fluorescent screen at B. Then under the effect of electric field, they strike at point A. Similarly they strike at point C under the influence of magnetic field only. Now electric and magnetic fields were adjusted in such a way that the electron again strike at point B.

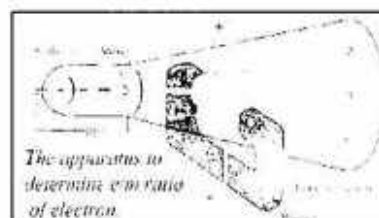


Fig. 2.4 Cathode rays in electric and magnetic rays

In this way by comparing the strength of the two fields, he determined the e/m value of an electron which is 1.7588×10^{11} Coulombs kg^{-1} . This means that 1 kg of electrons have 1.7588×10^{11} Coulombs of charge.

Measurement of charge on Electron (Millikan's oil drop experiment 1909)

R.A. Millikan Succeeded in measuring the charge of electron with great precision in 1909. Millikan constructed a box which consisted of two chambers. The upper chamber was filled with air whose pressure was adjusted by a vacuum pump. There were installed two electrodes A and A'. The electrodes were attached with electricity to generate an electric field in the space between the electrodes. The upper electrode had a hole in it as shown in the diagram. A fine spray of oil droplets was created

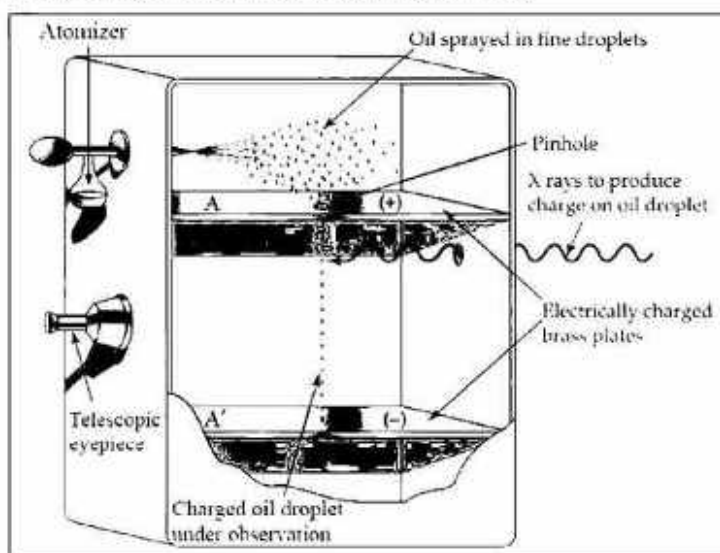


Fig. 2.5: Millikan's oil drop experiment



by an atomizer. Few droplets entered the hole. Then the hole was closed. An arc lamp was used to illuminate the space between the electrodes. The droplet fell under the force of gravity. The velocity (V_1) of the droplet was determined depending upon its weight.

$$V_1 \propto m \times g \quad \text{----- (1)}$$

Where m is mass of particle and g is acceleration due to gravity.

After that the air between the electrodes was ionized by X-rays. The droplet under observation took up an electron and got charged. Then A and A' were connected to a battery which generated an electric field having a strength E . The droplet moved upwards against gravitational force with a velocity V_2 .

$$\text{i.e.} \quad V_2 \propto E \times e - m \times g \quad \text{-----(2)}$$

Where E is strength of electric field and e is charge on electron.

Dividing Eq. (2) by Eq. (1)

$$\frac{V_1}{V_2} = \frac{mg}{Ee - mg}$$

If V_1 , V_2 , g and E are known, mass of an electron can be determined by varying the electric field in such a way that the droplet is suspended in the chamber. Hence " e " can be calculated which is 1.6022×10^{-19} coulombs.

Determination of Mass of an Electron

$$\text{We know that} \quad \frac{e}{m} = 1.7588 \times 10^{11} \text{Coulomb kg}^{-1}$$

$$\text{but} \quad e = 1.6022 \times 10^{-19} \text{Coulomb}$$

$$\therefore \quad \frac{1.60 \times 10^{-19} \text{C}}{m} = \frac{1.7588 \times 10^{11} \text{Ckg}^{-1}}{1}$$

$$\text{or} \quad m \times 1.7588 \times 10^{11} \text{C kg}^{-1} = 1.60 \times 10^{-19} \text{C}$$

$$m = \frac{1.60 \times 10^{-19} \text{C}}{1.7588 \times 10^{11} \text{Ckg}^{-1}}$$

$$m = 9.1095 \times 10^{-31} \text{kg}$$

Example 2.1 How much heavier is the H-atom as compared to an electron?

Solution: as we know that

$$\text{Mass of H atom} = 1.6736 \times 10^{-27} \text{ kg}$$

$$\text{Mass of electron} = 9.1095 \times 10^{-31} \text{ kg}$$

$$\frac{\text{Mass of H-atom}}{\text{Mass of electron}} = \frac{1.6736 \times 10^{-27} \text{ kg / H atom}}{9.1095 \times 10^{-31} \text{ kg / electron}} = \frac{1837}{1}$$

Hence Hydrogen atom is 1837 times heavier than an electron.

In 1886 Goldstein, a German Physicist discovered proton in cathode ray tube.

In a discharge tube, atoms or molecules lose electrons forming positive ions. Typical example is of ionization of Neon gas.

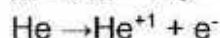
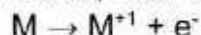


It is observed that the positive ions move towards cathode in a discharge tube.

Construction and Working

About one metre long tube was taken which was provided with a perforated cathode as shown in the diagram. The electrodes were connected to a high voltage battery.

Atom being electrically neutral must contain equal number of positive and negative particles. When electric current was passed through the gas under reduced pressure, some rays are produced from cathode which traveled away from cathode. Such rays ionize the gas in the middle of the discharge tube. They knocked out electron from the gas molecules. As a result positive ions were produced, which start moving towards the perforated cathode.



Since these rays passed through the canals (small holes) of cathode so they were also called as "Canal rays". Later on they were called Positive rays because they carried positive charge.

Properties of Positive Rays

Positive rays have the following properties:

- 1) They travel in straight line perpendicular to the anode surface.
- 2) They can be deflected by electric field.
- 3) Their deflection is towards cathode showing that they are positively charged.
- 4) They produce flashes on ZnS plate.
- 5) Their $\frac{e}{m}$ ratio is smaller than that of an electron.
- 6) The $\frac{e}{m}$ ratio depends upon the nature of the gas. The highest $\frac{e}{m}$ is obtained if Hydrogen gas is present in the tube.
- 7) The mass of a +ive particle is never less than that of a proton.
- 8) The positive particle obtained from H_2 gas is the lightest among all the positive particles.
- 9) A particle obtained from positive rays is called proton, a name suggested by Rutherford.
- 10) The mass of a proton is 1837 times more than that of an electron.

As proton is present in all the atoms therefore proton is a common constituent of all matter.

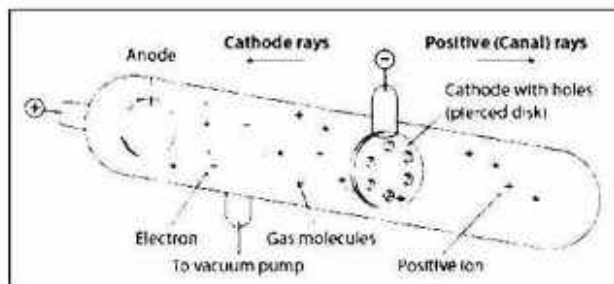


Fig. 2.6 Positive particles moving towards cathode in a discharge tube.

2.2 DISCOVERY OF NEUTRONS

After the discovery of electrons and protons in an atom, nothing extra was known about it until 1932. Rutherford in 1920 predicted that some neutral particles must also be present in it because he noticed that atomic mass of atoms could not be explained if it were supposed that atoms had only electrons and protons.

James Chadwick in 1932 performed an experiment and proved that certain neutral particles also exist in nucleus of an atom and he was awarded Nobel Prize in Physics in 1935 for this discovery.



James Chadwick

Experiment by James Chadwick

A stream of α -particles produced from Polonium (Po) was directed at target metal foil ${}^9_4\text{Be}$.

It was noticed that some penetrating radiations were produced. These radiations were called neutrons, because the charge detector showed them to be neutral.

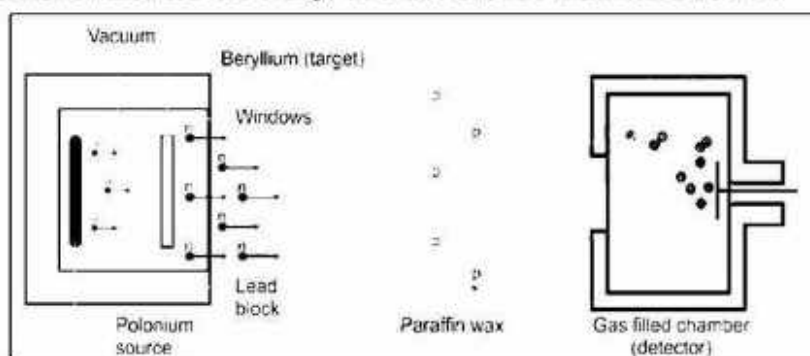


Fig. 2.7: α – rays bombarded on Beryllium sheet

The nuclear reaction is as follows:

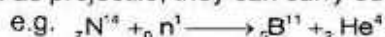


Properties of neutrons

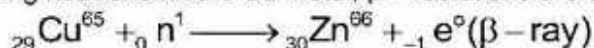
Neutrons have the following properties,

1. Free neutron decays into a proton with the emission of electron and neutrino.

$${}_0^1\text{n} \longrightarrow {}_1^1\text{p} + {}_{-1}^0\text{e} + {}_0^0\text{n} (\text{neutrino, particle of a small mass}).$$
2. They cannot ionize gases.
3. They are highly penetrating particles.
4. When neutrons travel with energy 1.2 MeV or more, they are called **Fast Neutrons**. And when have energy below 1 e.V., they are called **slow neutrons**.
5. They are not deflected in electric and magnetic fields. Hence they are neutral in nature.
6. They can knockout high speed protons from paraffins, water, paper and cellulose.
7. Slow neutrons are more effective than the fast ones for the fission purposes.
8. When neutrons are used as projectile, they can carry out the nuclear reactions.



When slow moving neutrons hit the Cu metal, β – radiations are emitted.



Because of their intense biological effects, they are used in the treatment of cancer.

2.3 THE DISCOVERY OF NUCLEUS (RUTHERFORD'S EXPERIMENT, 1910 – 11)

After the discovery of electron, proton and neutron in an atom, the next problem was to locate their positions. Rutherford in 1910 performed an experiment by bombarding α -particles (${}^4_2\text{He}$) from a radioactive element (Ra or Po) on a thin metallic foil (0.00004 cm thick) as shown by Fig 2.8. He observed that most of the α -particles passed un-deflected. A few were deflected through various angles and a very few of them were deflected in backward direction as shown by Fig 2.8.

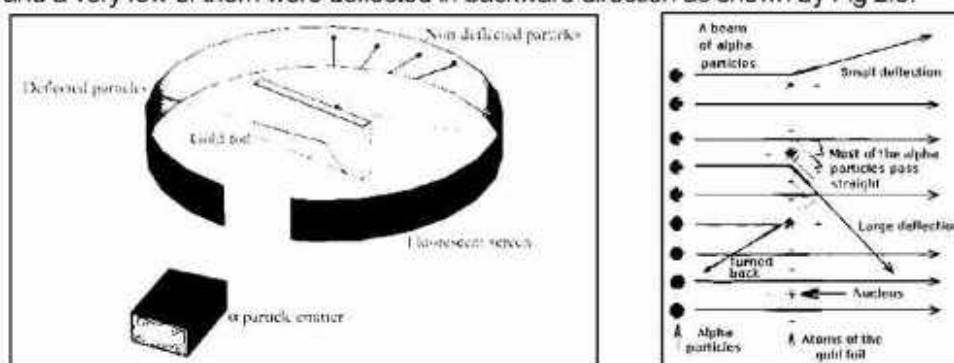


Fig. 2.8: α -rays bombarded on gold foil

Rutherford's Conclusions (Rutherford's Atomic Model)

1. An atom consists of a small heavy positively charged portion called Nucleus.
2. There is a negatively charged portion which surround the nucleus containing electrons called extra – nuclear portion or planetary.
3. The number of protons in the nucleus are equal to the number of electrons in the planetary.
4. The electrons revolve around the nucleus.
5. The centripetal force is equal to the electrostatic force.
6. Only a very small volume is occupied by the nucleus.

Defects of Rutherford Atomic Model

The defects of Rutherford Atomic Model are:

1. Rutherford Atomic Model is based upon laws of motion and gravitation which are applicable to neutral bodies but not to the charge bodies like electron and proton.
2. According to Maxwell's theory any charge particle moving in a circular path must radiate energy continuously and ultimately the electron must be spiral into the nucleus and the atom will collapse.
3. If electron emits energy continuously, it should form continuous spectrum. But actually, a line spectrum is obtained.

Table 2.1: Properties of Subatomic Particles

Particle	Charge/Coulomb	Relative charge	Mass/Kg	Mass(a.m.u)	Where found
Proton	$+ 1.6022 \times 10^{-19}$	+ 1	1.6727×10^{-27}	1.0073	In the nucleus
Neutron	0	0	1.6750×10^{-27}	1.0087	In the nucleus
Electron	$- 1.6022 \times 10^{-19}$	-1	9.1095×10^{-31}	5.4858×10^{-4}	Outside nucleus

2.4 BOHR'S ATOMIC MODEL AND ITS APPLICATIONS

In order to remove the defects of Rutherford atomic model and the investigate the internal structure of an atom, Neil Bohr, an English scientist (1913) proposed another possible structure of an atom called Bohr's atomic model. According to this model;

1. Electrons revolve around the nucleus in definite energy levels called orbits or shells.
2. As long as an electron remain in a shell it never gains or losses energy.
3. The gain or loss of energy occurs within orbits only due to jumping of electrons from one energy level to another energy level.

$$\Delta E = E_2 - E_1$$

4. Angular momentum (mvr) of an electron is equal to $nh/2\pi$.

The angular momentum of an orbit depends upon its quantum number and it is an integral multiple of the factor $h/2\pi$

i.e. $mvr = nh/2\pi$ Where $n = 1, 2, 3, \dots$

Bohr derived expressions for the calculations of radius of

n th orbit of an atom of hydrogen or ions like He^{+1} , Li^{+2} etc.

Let us consider an atom having an electron (e^-) moving around the nucleus having charge $Z e^+$, where Z is the atomic number. Let m be the mass of electron, r the radius of the orbit and v is the velocity of the revolving electron.

According to coulomb's law, the electrostatic force or

$$\text{Coulomb's force of attraction} = \frac{Ze^+ \times e^-}{4\pi\epsilon_0 r^2} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

Where ϵ_0 (the vacuum permittivity constant) = $8.84 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$.

$$\text{Centrifugal force acting on the moving electron} = \frac{mv^2}{r}$$

These two forces are equal and opposite and balance each other. So,

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \dots\dots\dots (1)$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$r = \frac{Ze^2}{4\pi\epsilon_0 mv^2} \dots\dots\dots (2)$$

Thus we conclude that the radius of a moving electron is inversely proportional to the square of its velocity.

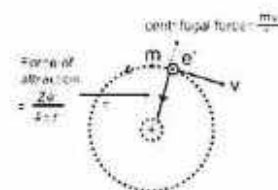


Figure 2.9 Electron revolving in an atom



Now we consider angular momentum. According to Neil Bohr,

$$mvr = \frac{nh}{2\pi} \quad \dots\dots\dots (3)$$

$$v = \frac{nh}{2\pi mr}$$

Taking square on both sides,

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad \dots\dots\dots (4)$$

Putting this value of v^2 in (2),

$$r = \frac{Ze^2}{4\pi\epsilon_0 m} \frac{4\pi^2 m^2 r^2}{n^2 h^2}$$

$$\frac{1}{r} = \frac{Ze^2 \pi m}{\epsilon_0 h^2 n^2}$$

$$\text{or } Ze^2 \pi m r = \epsilon_0 n^2 h^2$$

$$r = \epsilon_0 n^2 h^2 / Ze^2 m \pi \quad \dots\dots\dots (5)$$

For hydrogen, $Z = 1$

$$\text{So, } r = \frac{\epsilon_0 n^2 h^2}{\pi m e^2} \quad \dots\dots\dots (6)$$

$$\text{or } r = n^2 a_0$$

where $a_0 = \frac{\epsilon_0 h^2}{\pi m e^2}$, a constant quantity having a value of

$$0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA} \quad (\text{where } 1 \text{ \AA} = 10^{-10} \text{ m})$$

$$\text{So } r = n^2 \times 0.529 \text{ \AA}$$

Therefore radius of orbits having $n = 1, 2, \dots$ are as follows.

$$\text{When } n = 1, r = 1^2 \times 0.529 \text{ \AA} = 0.529 \text{ \AA}$$

$$\text{When } n = 2, r = 2^2 \times 0.529 \text{ \AA} = 4 \times 0.529 \text{ \AA} = 2.116 \text{ \AA}$$

3.3.2. ENERGY OF AN ELECTRON IN AN ORBIT

The energy of an electron in an orbit is the sum of its potential energy and kinetic energy.

$$\therefore E_{\text{Total}} = \text{K.E} + \text{P.E.}$$

$$= \left(\frac{1}{2} mv^2 \right) + \left(- \frac{Ze^2}{4\pi\epsilon_0 r} \right) \quad \dots\dots\dots (7)$$

$$E_{\text{Total}} = \frac{1}{2} mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

This potential energy is governed by the coulomb's Law of Electrostatic force.

Putting the value of mv^2 from eq. (1) into eq. (7)

$$\begin{aligned} E_{\text{Total}} = E_n &= \frac{1}{2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} \\ &= \frac{Ze^2}{4\pi\epsilon_0 r} \left(\frac{1}{2} - 1 \right) = \frac{Ze^2}{4\pi\epsilon_0 r} \left(-\frac{1}{2} \right) \\ &= -\frac{Ze^2}{8\pi\epsilon_0 r} \end{aligned} \quad \dots\dots\dots (8)$$

Now putting the value of r from eq. (5) in to eq. (8)

$$\begin{aligned} E_n &= -\frac{Ze^2}{8\pi\epsilon_0} \times \left[\frac{\pi m Z e^2}{\epsilon_0 n^2 h^2} \right] \\ &= -\frac{mZ^2 e^4}{8\epsilon_0 n^2 h^2} \end{aligned} \quad \dots\dots\dots (9)$$

For Hydrogen atom; $Z = 1$

$$\begin{aligned} \therefore E_n &= -\frac{me^4}{8\epsilon_0 n^2 h^2} \\ &= -\frac{me^4}{8\epsilon_0 h^2} \left[\frac{1}{n^2} \right] \end{aligned}$$

But $\frac{me^4}{8\epsilon_0 h^2} = 2.18 \times 10^{-18} \text{ J}$

This value is obtained by putting the values of constants.

$$\begin{aligned} \therefore E_n &= -2.18 \times 10^{-18} \left[\frac{1}{n^2} \right] \text{ J} \quad \dots\dots\dots (10) \\ &= -\frac{k}{n^2} \quad \text{where } k = 2.18 \times 10^{-18} \text{ J} \end{aligned}$$

The negative sign indicates decrease in energy of the electron.

The value of energy obtained is in Joules/atom. If this quantity is multiplied by Avogadro's No. and divided by 1000, the value of E_n becomes.

$$E_n = -\frac{1313.35}{n^2} \text{ kJ / mole.}$$

This energy is associated with 1.008 gram-atoms of hydrogen.

If $n = 1, 2, 3, 4, 5, \dots$

then

$$\begin{aligned} E_1 &= -\frac{1313.35}{1^2} = -1313.35 \text{ kJ mole}^{-1} \\ E_2 &= -\frac{1313.35}{2^2} = -328.32 \text{ kJ mole}^{-1} \\ E_3 &= -\frac{1313.35}{3^2} = -145.92 \text{ kJ mole}^{-1} \\ E_4 &= -\frac{1313.35}{4^2} = -82.08 \text{ kJ mole}^{-1} \\ E_5 &= -\frac{1313.35}{5^2} = -52.53 \text{ kJ mole}^{-1} \end{aligned}$$

The first energy level when $n = 1$ is known as the ground state of the hydrogen atom. All other energy levels are known as excited states.

According to Eq. (9) $E = -\frac{mZ^2e^4}{8\epsilon_0^2n^2h^2}$

Let E_1 be the energy of the lower energy orbit n_1 and E_2 that of higher energy orbit n_2 ,

Then
$$\begin{aligned}\Delta E &= E_2 - E_1 \\ &= \left(-\frac{mZ^2e^4}{8\epsilon_0^2n_2^2h^2} \right) - \left(-\frac{mZ^2e^4}{8\epsilon_0^2n_1^2h^2} \right) \\ &= -\frac{mZ^2e^4}{8\epsilon_0^2n_2^2h^2} + \frac{mZ^2e^4}{8\epsilon_0^2n_1^2h^2} \\ &= \frac{mZ^2e^4}{8\epsilon_0^2n_1^2h^2} - \frac{mZ^2e^4}{8\epsilon_0^2n_2^2h^2} \\ &= \frac{mZ^2e^4}{8\epsilon_0^2h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]\end{aligned}$$

For Hydrogen, $Z = 1$

$$\therefore \Delta E = \frac{me^4}{8\epsilon_0^2h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots\dots\dots (11)$$

Here, $\frac{me^4}{8\epsilon_0^2h^2} = 2.18 \times 10^{-18} \text{ J.}$

$$\therefore \Delta E = 2.18 \times 10^{-18} \text{ J} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots\dots\dots (12)$$

According to Plank's Quantum theory,

$$\Delta E = h\nu$$

$$\therefore h\nu = 2.18 \times 10^{-18} \text{ J} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right].$$

$$\text{again } h\nu = \frac{me^4}{8\epsilon_0^2h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{or } \nu = \frac{me^4}{8\epsilon_0^2h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ Hz or cycles sec}^{-1} \quad \dots\dots\dots (13)$$

The relationship between frequency (ν) and wave number ($\bar{\nu}$) is

$$\nu = \bar{\nu}c \quad \dots\dots\dots (14)$$

Where c is the velocity of light.

Putting the value of ν from eq. (13) in eq. (14)

$$\bar{\nu}c = \frac{Z^2 me^4}{8\epsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

or
$$\bar{\nu} = \frac{Z^2 me^4}{8\epsilon_0^2 h^3 c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots\dots\dots (15)$$

Putting values of constants, $\frac{me^4}{8\epsilon_0^2 h^3 c} = R = 1.09678 \times 10^7 \text{ m}^{-1}$,
 R called Rydberg's constant?

$$\bar{\nu} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots\dots\dots (16)$$

$$\therefore \bar{\nu} = 1.09678 \times 10^7 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ m}^{-1}$$

Example 2.2

Calculate the value of a_0 of H – atom.

Solution

We know that $a_0 = \frac{\epsilon_0 h^2}{\pi m e^2}$

The values of the constant are:

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$\pi = 3.142$$

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$e = 1.60 \times 10^{-19} \text{ C.}$$

Putting these values in equation, $a_0 = \frac{\epsilon_0 h^2}{\pi m e^2}$

$$\begin{aligned} a_0 &= \frac{8.854 \times 10^{-12} \times (6.626 \times 10^{-34})^2}{3.142 \times 9.11 \times 10^{-31} \times (1.60 \times 10^{-19})^2} \\ &= 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ \AA} \end{aligned}$$

Example 2.3

Calculate the radius of 3rd orbit of electron in H-atom.

Solution

$$r_n = a_0 n^2$$

As $a_0 = 5.29 \times 10^{-11} \text{ m.}$ and $n = 3$

$$\begin{aligned} \therefore r^3 &= (3)^2 \times 5.29 \times 10^{-11} \text{ m} \\ &= 9 \times 5.29 \times 10^{-11} \text{ m} \\ &= 47.61 \times 10^{-11} \text{ m} = 4.761 \text{ \AA} \end{aligned}$$

Example 2.4

Calculate energies of n_1 for (i) ${}_2\text{He}^+$ (ii) ${}_3\text{Li}^{+2}$

Solution:

$$E_n = -\frac{k Z^2}{n^2} \quad \text{where} \quad k = \frac{e^4 m}{8\epsilon_0^2 h^2 n^2}$$



(i) $Z = 2$ for ${}_2\text{He}^+$,
 Then $E_{n_k} = -\frac{(2)^2 k}{1^2}$
 or $E_{1st} = -\frac{4 \times 2.18 \times 10^{-18}}{1} = -8.72 \times 10^{-18} \text{ J}.$

(ii) $Z = 3$ for ${}_3\text{Li}^{+2}$
 $E_{1st} = -\frac{(3)^2 k}{1^2}$ $E_{1st} = -\frac{9 \times 2.18 \times 10^{-18} \text{ J}}{1}$
 $= -1.962 \times 10^{-17} \text{ J}.$

Example 2.5

How much energy is required to make electron of H-atom to jump from $n = 2$ to $n = 4$.

Solution:

Here $\Delta E = E_{\text{Final}} - E_{\text{Initial}}$
 $n_1 = 2,$ & $n_2 = 4$
 (lower energy orbit) (higher energy orbit)

So $\Delta E = k \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$
 $= k \left[\frac{1}{4} - \frac{1}{16} \right]$
 $= k \left[\frac{4-1}{16} \right]$

But $k = 2.18 \times 10^{-18} \text{ J}.$
 $\therefore \Delta E = 2.18 \times 10^{-18} \times \frac{3}{16}$
 $= 4.08 \times 10^{-19} \text{ J}$

**Self Check Exercise 2.1**

- Calculate how much energy is required in order to remove electron of hydrogen atom. (Ans: $2.18 \times 10^{-18} \text{ J}$)
 (Hint consider $n_1 = 1, n_2 = \infty$)
- Convert this energy into ν and λ (Ans: $3.288 \times 10^{15} \text{ s}^{-1}, 1.096 \times 10^7 \text{ m}^{-1}$)

Limitations of Bohr's atomic model

- Bohr's atomic model is applicable to one electron system and cannot explain the origin of the spectrum of multi-electrons or polyelectronic systems like He, Li, Be etc.
- When a spectrum of Hydrogen gas is seen through a powerful spectrometer, the origin of spectral lines are replaced by several very fine lines. i.e., original lines are divided into other fine lines. Bohr's theory cannot explain this fine structure.
- Bohr suggested circular orbits of electrons around the nucleus of H-atom. But it is proved that the motion of electron is not in a single plane, but takes place in three-dimensional space.
- Bohr's theory cannot explain the effect of magnetic field (Zeeman Effect) and electric field (Stark Effect) on the spectra of atoms.

Zeeman's Effect:

"The splitting of spectral lines of H-spectrum under the influence of magnetic field."

Stark's Effect:

"The splitting of spectral lines of H-spectrum under the influence of electric field."

Bohr's picture of an atom is not satisfactory. In Bohr's atom, the electrons are moving in orbits with specific velocities in specific radii. But according to **Heisenberg's uncertainty principle**, both the exact position and velocity of electron cannot be measured simultaneously. In order to solve this difficulty, Schrodinger gave a wave equation for hydrogen atom. According to him, although the position and velocity of an electron cannot be found exactly, the probability of finding an electron can be ascertained. The maximum probability is at a distance of 0.0529 nm.

The visual display or dispersion of the components of visible light, when it is passed through a prism is called spectrum. These are two types of spectrum:

(a) Continuous Spectrum:

When the boundary lines between the colors cannot be marked it is called continuous spectrum.

(b) Line Spectrum:

When the boundary lines between the colors are separately isolated and marked it is called line spectrum.

When Hydrogen is enclosed in a container and heated, it emits radiation. These radiation are actually emitted due to excitation and de-excitation of electron of hydrogen.

According to equation 16,

$$\bar{\nu} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] m^{-1}$$

With this equation, Bohr was able to predict the wave number in the hydrogen emission spectrum and the electron transition (changes of energy levels) that occur in hydrogen atom.

The wave number of different spectral lines can be calculated corresponding to the values of n_1 and n_2 . In the hydrogen spectrum, different series of lines have been identified for n_1 and n_2 values. These series are,

Lyman series	n_1	=	1	n_2	=	2,3,4,5 ...
Balmer series	n_1	=	2	n_2	=	3,4,5,6 ...
Paschen series	n_1	=	3	n_2	=	4,5,6,7 ...
Brackett series	n_1	=	4	n_2	=	5,6,7,8 ...
Pfund series	n_1	=	5	n_2	=	6,7,8,9 ...

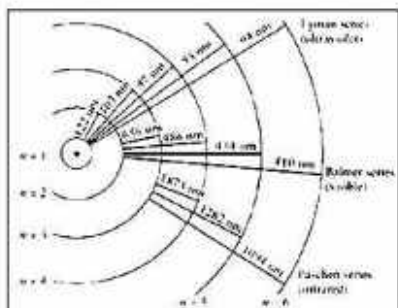


Fig. 2.10: Spectrum of hydrogen atom showing electronic transition to give different series

Only the Balmer series was observed in the visible part of the spectrum. Lyman series lie in the ultraviolet region while the Paschen, Brackett and Pfund series have been observed in the infrared region.

Origin of Hydrogen Spectrum on the Basis of Bohr's Model.

The first spectral lines were discovered in 1887 by Lyman and Balmer. No satisfactory reason became available till 1913. Neil Bohr presented his explanation of line spectra in 1913.

According to Bohr when current is passed through the hydrogen gas in the discharge tube at low pressure, the molecules of hydrogen break into atoms. These atoms absorb energy from the electric spark. The electrons of hydrogen atoms are excited to high energy levels. The higher energy orbits to which the electron migrates depend upon the amount of energy absorbed by the electron. Above diagram shows the possibilities of movement of electron from lower to higher levels.

These excited electrons being unstable come back to one of the lower energy levels. The electrons may come to the lowest energy levels. In this way they emit energy, they had absorbed. Lyman series is produced when the electrons jump from $n=2,3,4,5,6...$ etc to $n=1$. In Balmer series the electrons from $n=3,4,5,6...$ come back to $n=2$.

Let us calculate the various lines of Lyman series, Balmer series, Paschen series, Brackett series and Pfund series from Bohr's equation of wave number.

$$\bar{\nu} = 1.09678 \times 10^7 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{m}^{-1}$$

Lyman Series

The various lines in Lyman series got their explanation by considering that the electrons of hydrogen atom fall back to $n=1$ from higher levels. The higher levels occupied by the electrons due to the electric spark.

First line: $n_1 = 1$ $n_2 = 2$
 $\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \text{m}^{-1} = 82.26 \times 10^5 \text{m}^{-1}$

Second line: $n_1 = 1$ $n_2 = 3$
 $\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{3^2} \right) \text{m}^{-1} = 97.60 \times 10^5 \text{m}^{-1}$

Third line: $n_1 = 1$ $n_2 = 4$
 $\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2} \right) \text{m}^{-1} = 102.70 \times 10^5 \text{m}^{-1}$

Limiting line: $n_1 = 1$ $n_2 = \infty$
 $\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) \text{m}^{-1} = 109.678 \times 10^5 \text{m}^{-1}$

This limiting line shows that the energy difference between the first level and the infinite level is the ionization energy of the hydrogen atom. All these lines of Lyman series have close values. They appear in the form of a group. These values of wave numbers lie in the UV region of the spectrum.

Balmer series:

In this series the electrons fall back to **n=2**.

First line (Hα line):	$n_1 = 2$	$n_2 = 3$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \text{m}^{-1} = 15.234 \times 10^5 \text{m}^{-1}$
Second line (Hβ line):	$n_1 = 2$	$n_2 = 4$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \text{m}^{-1} = 20.566 \times 10^5 \text{m}^{-1}$
Third line (Hγ line):	$n_1 = 2$	$n_2 = 5$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{5^2} \right) \text{m}^{-1} = 23.05 \times 10^5 \text{m}^{-1}$
Limiting line:	$n_1 = 2$	$n_2 = \infty$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) \text{m}^{-1} = 27.421 \times 10^5 \text{m}^{-1}$

All these lines of Balmer series are very close to each other and appear in the form of group of lines. These lines lie in the visible region of the spectrum.

Paschen Series:

The electrons from higher levels fall back to **n=3**.

First line:	$n_1 = 3$	$n_2 = 4$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{4^2} \right) \text{m}^{-1} = 5.3310 \times 10^5 \text{m}^{-1}$
Second line:	$n_1 = 3$	$n_2 = 5$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{5^2} \right) \text{m}^{-1} = 7.799 \times 10^5 \text{m}^{-1}$
Limiting line:	$n_1 = 3$	$n_2 = \infty$	$\bar{\nu} = 1.09678 \times 10^7 \left(\frac{1}{3^2} - \frac{1}{\infty^2} \right) \text{m}^{-1} = 12.187 \times 10^5 \text{m}^{-1}$

These are again the groups of lines close to each other and appear in IR region.

Brackett series:

The electrons from higher levels fall back to **n=4**.

First line:	$n_1 = 4$	$n_2 = 5$	$\bar{\nu} = 2.45 \times 10^5 \text{m}^{-1}$
Second line:	$n_1 = 4$	$n_2 = 6$	$\bar{\nu} = 3.808 \times 10^5 \text{m}^{-1}$
Limiting line:	$n_1 = 4$	$n_2 = \infty$	$\bar{\nu} = 6.855 \times 10^5 \text{m}^{-1}$

Pfund series:

The electrons from higher energy levels fall back to **n=5**.

First line:	$n_1 = 5$	$n_2 = 6$	$\bar{\nu} = 1.340 \times 10^5 \text{m}^{-1}$
Second line:	$n_1 = 5$	$n_2 = 7$	$\bar{\nu} = 2.148 \times 10^5 \text{m}^{-1}$
Limiting line:	$n_1 = 5$	$n_2 = \infty$	$\bar{\nu} = 4.387 \times 10^5 \text{m}^{-1}$

2.5 PLANK'S QUANTUM THEORY

Max Plank (1900) proposed a theory about nature of light. According to this theory,

- Energy is not emitted or absorbed continuously. It is emitted or absorbed in the form of wave packets or quanta. In case of light the quantum of energy is often called photon.
- The amount of energy associated with quantum of radiation is directly proportional to the frequency (ν) of radiation, i.e.

$$E \propto \nu \quad \text{or} \quad E = h \nu \quad \dots\dots\dots (1)$$

where h = Plank's constant and has a value of 6.625×10^{-34} Joules sec.

(c) A body can emit or absorb energy only in terms of integral multiple of a quantum.

$$E = nh\nu \quad \text{where } n = 1, 2, 3$$

Now $\nu \propto 1/\lambda$

or $\nu = c/\lambda$

Where " λ " is wave length and " c " is the velocity of light, a constant quantity.

Putting the value of ν in eq. (1), we get

$$E = hc/\lambda \quad \dots\dots\dots (2)$$

Thus greater the value of λ , smaller will be the energy.

Now $\bar{\nu} = 1/\lambda \quad \dots\dots\dots (3)$

Where $\bar{\nu}$ = wave number.

Putting the value of $1/\lambda$ in eq. (2), we get,

$$E = hc\bar{\nu}$$

Thus energy of radiation is directly proportional to the frequency.

So, it can be concluded that the energy of photon is related to frequency, wavelength and wave number. **The number of waves passing through a point per second is called Frequency. The distance between two adjacent crests or troughs is called wavelength.** It is expressed in Å (Where Å is an angstrom and one Angstrom = 10^{-10}m) or in nanometers (1 nanometre = 10^{-9}m).

Example 2.6

A photon of light with energy 10^{-19}J is emitted by a source of light.

- Convert this light in to the wave length, frequency and wave number of the photon in terms of meters, Hertz and m^{-1} , respectively.
- Convert this energy of photon into ergs and calculate the wavelength in cm, frequency in Hz and wave number in cm^{-1} .

Solution: (a)

Data:	Energy of photon		$= 10^{-19}\text{J}$
	Wavelength	$= \lambda$	$= ?$
	Frequency	$= \nu$	$= ?$
	Wave number	$= \bar{\nu}$	$= ?$

First of all we calculate ν

Formula applied:

$$\begin{aligned}
 E &= h\nu \\
 \text{and } \nu &= \frac{E}{h} \\
 h &= 6.625 \times 10^{-34}\text{Js}
 \end{aligned}$$

Putting the values of E and h

$$\begin{aligned}
 \nu &= \frac{10^{-19}\text{J}}{6.625 \times 10^{-34}\text{Js}} \\
 &= 0.151 \times 10^{15}\text{s}^{-1} \\
 &= 1.51 \times 10^{14}\text{s}^{-1}
 \end{aligned}$$

From ν we can calculate wavelength λ



Formula applied:

$$\begin{aligned} \nu &= \frac{c}{\lambda} \\ \text{So, wavelength } \lambda &= \frac{c}{\nu} \\ &= \frac{3 \times 10^8 \text{ ms}^{-1}}{1.51 \times 10^{14} \text{ s}^{-1}} \\ \lambda &= 1.98 \times 10^{-6} \text{ m} \end{aligned}$$

From λ , we can calculate wave number

Formula applied:

$$\begin{aligned} \text{Wave number } \tilde{\nu} &= \frac{1}{\lambda} \\ \tilde{\nu} &= \frac{1}{1.98 \times 10^{-6} \text{ m}} \\ \tilde{\nu} &= 0.50 \times 10^6 \text{ m}^{-1} \\ &= 5 \times 10^5 \text{ m}^{-1} \end{aligned}$$

(b) Now we convert energy of the photon from joules into ergs;

$$\begin{aligned} 1 \text{ J} &= 10^7 \text{ erg} \\ \text{So } E &= 10^{-19} \times 10^7 \text{ erg} = 10^{-12} \text{ ergs} \\ h &= 6.625 \times 10^{-27} \text{ erg} \times \text{s or erg.s} \end{aligned}$$

Now calculate frequency in Hz

Formula applied:

$$\begin{aligned} \nu &= \frac{E}{h} \\ \text{Putting the values} \\ \nu &= \frac{10^{-12} \text{ ergs}}{6.625 \times 10^{-27} \text{ erg.s}} \\ \nu &= 0.151 \times 10^{15} \text{ s}^{-1} \\ &= 1.51 \times 10^{14} \text{ s}^{-1} \end{aligned}$$

Now we can calculate wavelength in cm

Formula applied:

$$\begin{aligned} \lambda &= \frac{c}{\nu} \\ \text{Putting the values} \\ \lambda &= \frac{3 \times 10^{10} \text{ cms}^{-1}}{1.51 \times 10^{14} \text{ s}^{-1}} \\ &= 1.98 \times 10^{-4} \text{ cm} \end{aligned}$$

Now calculate wave number in cm^{-1}

Formula applied:

$$\begin{aligned} \tilde{\nu} &= \frac{1}{\lambda} \\ \tilde{\nu} &= \frac{1}{1.98 \times 10^{-4}} \\ &= 5 \times 10^3 \text{ cm}^{-1} \end{aligned}$$

2.6 X-RAYS

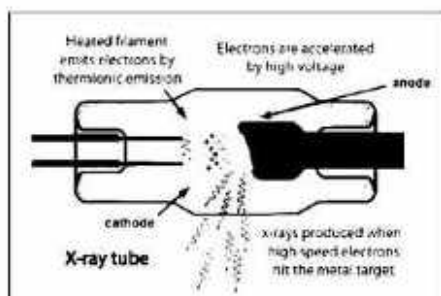


Figure 2.11: Cathode rays pointed at heavy metal (W, Cu etc.)

Wilhelm Roentgen (1895) accidentally discovered that if cathode rays are pointed to fall on a heavy metal target, there are produced some penetrating short wave length rays. He called them the X-rays. The X-rays are electromagnetic radiations of very high frequency depending upon the nature of anode. Oftenly a tungsten filament is used for this purpose.

X-rays are emitted from the target in all directions. A small portion of them is used for useful purpose through the windows. The wavelength of X-rays produced depends upon the nature of target metal. Every metal has its own characteristic X-rays.

Moseley undertook a systematic and comprehensive study of X-rays in 1913. His researches covered a range of wavelengths $0.04 - 0.08 \text{ \AA}$.

Moseley proved that the frequencies of X-rays increase in a regular manner from one element to the other in the Periodic Table. He further suggested that the frequencies of these rays are directly proportional to the no of protons in the nucleus. The no of protons in the nucleus is called "Atomic Number".

Moreover Moseley drew the following conclusions from the detailed analysis of spectral lines which he obtained from 38 different elements. (from Al to Au) as targets in X-rays tube.

- The spectral lines could be classified into two distinct groups. One, which belongs to shorter wavelength, called K-series and the other with longer wavelength called as L-series.
- If the target element is of higher atomic number the wave-length of X-rays becomes shorter.
- A relationship between frequency (ν) and atomic number (Z) of the elements is given as

$$\sqrt{\nu} = a(Z - b)$$

This is called **Moseley Law**. Where a and b are called constant quantities. **This law states that the frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it.**

In 1913 Henry G. J. Moseley, a student of Rutherford, used the technique of X-rays spectroscopy (just discovered by Max von Laue) to determine the atomic numbers of the elements, X-rays are produced in a cathode-ray tube when the electron beam (cathode ray) falls on a metal target. The explanation for the production of X-rays is as follows: When an electron in the cathode ray hits a metal atom in the target, it can (if it has sufficient energy) knock out an electron from an inner shell of the atom. This produces a metal ion with an electron missing from an inner orbital. The electronic configuration is unstable, and an electron from an orbital of higher energy drops in to the half-filled orbital and a photon is emitted. The photon corresponds to electromagnetic radiations in the x-ray region.

1. X-rays have different penetrating powers for different types of matter. X-rays cannot pass through metals, but they can pass through plastic, leather etc. easily. That's why they can be used for security purposes to photograph interior of objects.
2. They are used in medical radiography to locate fracture in the bones.
3. In England, in 1913 William Bragg and Lawrence Bragg used X-ray diffraction (XRD) technique to study the crystal structure.
4. X-rays can be used to ionize gases.

2.7 THE QUANTUM NUMBERS AND ORBITALS

Schrodinger in 1926 gave an equation in which electrons are treated as moving with wave like motion in the three dimensional space around the nucleus. It differs from Bohr's atomic model in the sense that the electrons move in orbits. It also specifies the distance between the electron and the nucleus.

The solution of Schrodinger's wave equation gives certain mathematical integers. **These sets of numerical values, which give the acceptable picture of an atom, are called Quantum Numbers.** There are four quantum numbers which can describe the electron completely.

1. Principal Quantum No. (n)

It determines the size of the orbit and the distance from the nucleus. Greater the distance from the nucleus, larger will be the size of the orbit. The shells are named as,

- if $n = 1$ — K shell.
 $n = 2$ — L shell.
 $n = 3$ — M shell.
 $n = 4$ — N shell.

The number of electrons accommodated in an orbit is given by $2n^2$.

The no of electrons accommodated in various orbits are as follows,

$$K = 2, \quad L = 8, \quad M = 18, \quad N = 32.$$

The higher the value of n , the higher will be the energy of the electron and space around the nucleus.

2. The Azimuthal Quantum No. (l)

It describes the shape of an orbital. Its value is always one less than that of value of n . The various energy sub-levels (l) are s, p, d, f having at the most 2, 6, 10 and 14 electrons in them respectively. They are designated as s for sharp, p for principal, d for diffused and f for fundamental. The values of l are:

$$l = 0, \dots, (n-1)$$

The maximum number of electrons in a subshell is given by a formula: $2(2l+1)$

If,	$n = 1$ (K),	$l = 0$ (s),	and $e = 2$
	$n = 2$ (L),	$l = 0$ (s) and 1 (p),	and $e = 2, 6$
	$n = 3$ (M),	$l = 0$ (s), 1(p), and 2(d)	and $e = 2, 6, 10$
	$n = 4$ (N),	$l = 0$ (s), 1(p), 2 (d) and 3 (f) and	$e = 2, 6, 10, 14$

From here we conclude that the number of orbit gives the no of orbitals.

i.e.	$n = 1$ (K)	orbital	= 1 s
	$n = 2$ (L)	orbitals	= 2s, 2p
	$n = 3$ (M)	orbitals	= 3s, 3 p, 3 d
	$n = 4$ (N)	orbitals	= 4s, 4p, 4d, 4f.

The shapes of orbitals described by Azimuthal Quantum number are s = spherical, p = dumbbell, d = sausage and f = complicated.

3. Magnetic Quantum No. (m)

It explains the effect of an orbital in the magnetic field. It is related with Azimuthal Quantum number as follows:

$$m = +l \longrightarrow 0 \longrightarrow -l$$

If $l = 0$ (s), $m = 0$. It means that an s-orbital is spherical in shape because it is not deflected in any particular direction on placing in a magnetic field.

If $l = 1$ (p), $m = +1, 0, -1$. It means that a p-orbital can be deflected in three directions on placing in a magnetic field. i.e. a p-orbital splits in to three degenerate orbitals in a magnetic field.

If $l = 2$ (d), then $m = +2, +1, 0, -1, -2$. It means that a d-orbital can be deflected in 5-directions on placing in a magnetic field.

If $l = 3$ (f), then, $m = +3, +2, +1, 0, -1, -2, -3$. i.e. an f-orbital can be deflected in 7-direction in a magnetic field.

The whole discussion shows that magnetic quantum number determines the orientation of orbital.

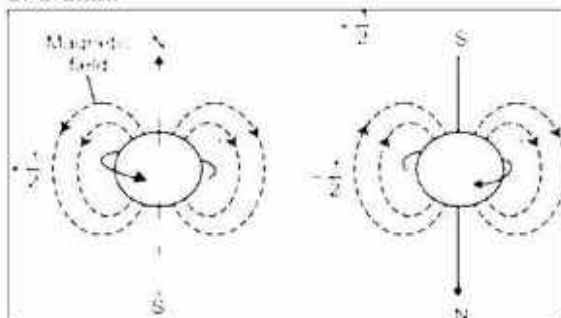


Figure 2.12: Two different spins of electrons and their magnetic fields

4. Spin Quantum Number (s)

It describes the direction of spin of an electron. In 1925 Goudsmit suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in a clockwise or anti-clockwise direction. It may be 50% clockwise $\left(-\frac{1}{2}\right)$ ($\uparrow$)

and 50% anti-clockwise $\left(+\frac{1}{2}\right)$ ($\downarrow$).

This is also called self-rotation. This spinning of electron is associated with a magnetic field and hence a magnetic moment.

The circular path of an electron around the nucleus is called an orbit. The orbits or shells are denoted by K, L, M, N etc. The orbits of an atom can be shown as in figure 2.13.

A cloud showing the probability of finding the electron in terms of charged cloud around the nucleus is called Electron Cloud.

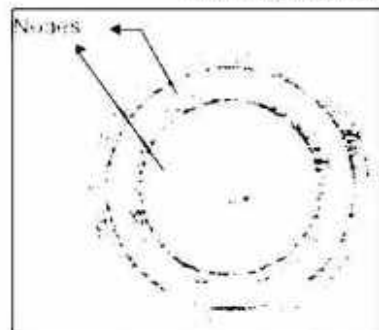


Figure 2.13: Shapes of orbits or shells

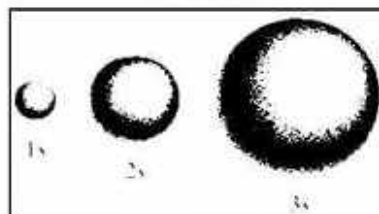


Figure 2.14: Shapes of s orbitals

The circular paths in which electrons revolve around the nucleus are called orbits or shells. An orbit or a shell consists of the orbitals or sub-shells.

Shapes of orbitals

s-orbital:

An s-orbital is spherical and symmetrical in shape.

With the increase of value of n , the size of s-orbital increases e.g. 2s orbital is larger in size than 1s – orbital. The probability of finding the electron is zero between two orbitals. This plane is called nodal plane or nodal surface.

p-orbitals:

A p-orbital is dumbbell in shape and has three directions in space. Such orbitals which have different directions but equal energy are called "Degenerate Orbitals".

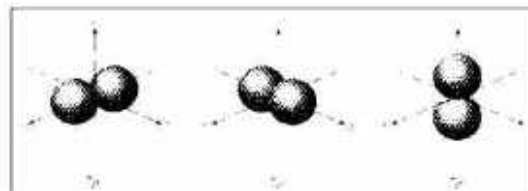


Figure 2.15: Shapes of p orbitals

d-orbitals:

These orbitals have dumbbell like structures and can move in the 5-directions. They are d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} .

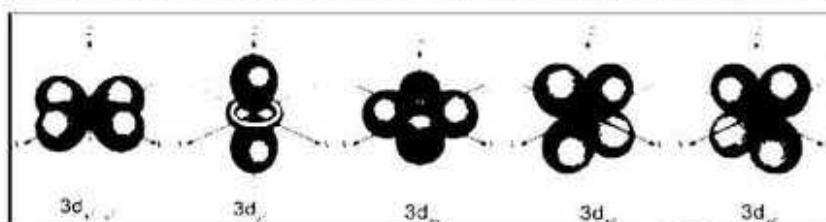


Figure 2.16: Shapes of d orbitals

In the absence of magnetic field all the five d-orbitals are degenerate.

f-orbitals:

It has seven directions in space on placing in a magnetic field, which are very complicated to draw.

Example 2.7

Describe the allowed combinations of the n , l and m quantum numbers when $n = 4$.

Solution:

The allowed combinations are

n	l	m
4	0	0
	1	-1, 0, +1
	2	-2, -1, 0, +1, +2
	3	-3, -2, -1, 0, +1, +2, +3

2.8 ELECTRONIC CONFIGURATIONS

The representation of filling of electrons in different orbitals of an atom is called its electronic configuration.

The relative energies depend upon the size of the orbitals and therefore, according to the *Principal Quantum Number* (n), an s-orbital has the lowest energy and increases as follows.

$$s < p < d < f$$

The relative energies are arranged in the figure 2.17.

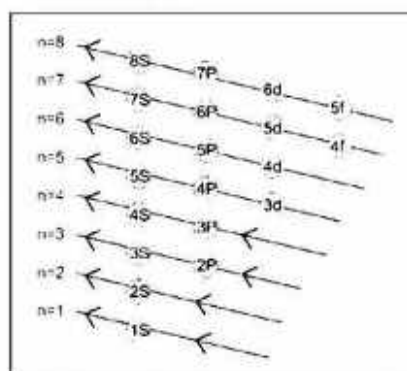


Figure 2.17: Energy sequence of different orbitals of an atom

The following facts must be observed before writing the electronic configuration of an atom.

- (a) An orbital like s , p_x , p_y , p_z , d_{xy} etc. can have maximum two electrons.
 (b) The energy order of an orbital is governed by " $n + l$ " rule, (where l -value is the value of Azimuthal Quantum number). This states that

- (i) An added electron will always enter in an orbit having lower $n + l$ value.

For example

2s,	$n = 2,$	$l = 0,$	$n + l = 2$
3d,	$n = 3,$	$l = 2,$	$n + l = 5$

So, 2s-orbital is filled first because it has lower value of $n + l$ than that for 3d orbital.

- (ii) If $n + l$ values of two orbitals are same, then the orbital with lower n value has lower energy and electron will be added to that orbital first. For example

4p,	$n = 4,$	$l = 1,$	$n + l = 5$
3d,	$n = 3,$	$l = 2,$	$n + l = 5$

But here 3d orbital is filled first because the value of n for 3d is smaller than that of 4p therefore an added electron would enter in 3d orbital first than that of 4p.

Auf-Bau Principle:

The electrons are placed in energy sub-levels in the order of increasing energy values of sub-levels.

Pauli's Exclusion Principle:

According to it "No two electrons in the same orbital can have the same set of four Quantum numbers.

Let us take the example of an orbital having two electrons.

For first electron: $n = 1,$ $l = 0,$ $m = 0,$ $s = +\frac{1}{2}$ ($\uparrow$)

For second electron: $n = 1,$ $l = 0,$ $m = 0,$ $s = -\frac{1}{2}$ ($\downarrow$)

So this orbital will have a maximum no. of two electrons with opposite spin i.e. ($\uparrow\downarrow$). Such an orbital is said to be completely filled and may contain a single electron in it, called as un-paired electron.

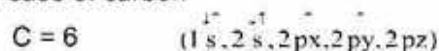
Hund's Rule:

If degenerate orbitals are available for electrons, then electron would like to live in separate orbitals and have rather parallel spin. It means that the arrangement $\uparrow\uparrow$ will be more stable than the arrangement $\uparrow\downarrow$, provided the two circles represent the orbitals of equal energies. The Hund's rule can be applied to predict the valency of an element because the numbers of unpaired electrons give the valency of that element. The rule is equally applicable in case of hybridized orbitals and molecular orbitals which are degenerate

e.g.	O = 8	($1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$)	Divalent
	N = 7	($1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$)	Trivalent
	Ne = 10	($1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$)	No valency or zero valency.



But in case of carbon



It looks divalent but actually it is tetravalent.

Example 2.8

Pick the orbital with the lower energy from each of the given pairs.

- (a) 3d, 4s, (b) 2p, 3s,

Solution:

We apply $n + l$ rule here,

(a) For 3d, $n = 3, \quad l = 2, \quad n + l = 5$

For 4s $n = 4, \quad l = 0, \quad n + l = 4$

So, 4s-orbital will be filled first because it has lower energy than that of 3d.

(b) For 2p, $n = 2, \quad l = 1, \quad n + l = 3$

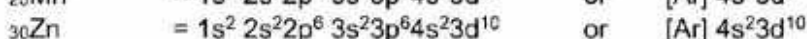
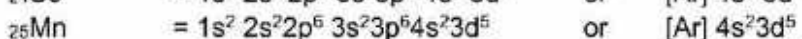
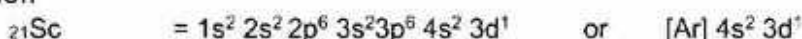
3s, $n = 3, \quad l = 0, \quad n + l = 3$

As the values of $n + l$ are equal in both the cases, therefore, 2p will be filled first than 3s.

Example 2.9

Write the electronic configuration of $_{21}\text{Sc}$, $_{25}\text{Mn}$, $_{30}\text{Zn}$.

Solution



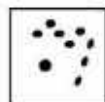
Self Check Exercise 2.2

Write the electronic configuration of following elements:

- (i) $_{20}\text{Ca}^{40}$ (ii) $_{17}\text{Cl}^{35}$ (iii) $_{13}\text{Al}^{27}$

References for additional information

- Philip Mathews, Advanced Chemistry.
- Martin S. Silberger, Chemistry, The molecular Nature of matter and change.
- John C. Kotz, Paul M. Treichel and Gabriela C. Weaver, Chemistry and chemical reactivity.
- E. N. Ramesden, A – Level chemistry.



1 Choose the correct answer (MCQs).

- For which species Bohr's theory does not apply;
(a) H (b) He^+ (c) Li^{2+} (d) Be
- From the discharge tube experiment, it is concluded that;
(a) Mass of a proton is in fraction. (b) Matter contained electrons.
(c) Nucleus contains positive charge. (d) Positive rays are heavier than protons.



- iii. When an electron of charge 'e' and mass 'm' moves with velocity 'v' about the nuclear charge Ze in the circular orbit of radius 'r', the P.E of electron is given by;
 (a) Ze^2/r (b) $-Ze^2/r$ (c) Ze^2/r^2 (d) mv^2/r
- iv. Which of following tell about shells of an atom?
 (a) Principal quantum number, n (b) Azimuthal quantum number, l
 (c) Magnetic quantum number, m (d) Spin quantum number, s
- v. Electronic configuration of species M^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ and its atomic weight is 56 number of neutrons in the nucleus of species M is
 (a) 20 (b) 26 (c) 28 (d) 30
- vi. The energy of an electromagnetic radiation is 3×10^{-12} ergs. What is its wave-length in nano meters?
 (a) 400 (b) 228.3 (c) 3000 (d) 662.5
- vii. Which of the following configuration is not correct according to Hund's rule?
 (a)

$\uparrow\downarrow$

$\uparrow\downarrow$	$\uparrow$	$\uparrow$
----------------------	------------	------------

 (b)

$\uparrow\downarrow$

$\uparrow$	$\uparrow$	
------------	------------	--

 (c)

$\uparrow\downarrow$

$\uparrow\downarrow$	$\uparrow$	
----------------------	------------	--

 (d)

$\uparrow\downarrow$

$\uparrow$	$\uparrow$	$\uparrow$
------------	------------	------------
- viii. Which one of the following statement is not correct?
 (a) Rydberg's constant and wave number have same unit.
 (b) Lyman series of hydrogen spectrum occurs in the ultraviolet region.
 (c) The angular movement of the electron in the ground state of hydrogen atom is equal to $h/2\pi$.
 (d) The radius of first Bohr orbit of hydrogen atom is 2.116×10^{-8} cm.
- ix. Which one of the following is not isoelectronic pair?
 (a) Mg^{2+} , Be^{2+} (b) N^{3-} , O^{2-} (c) N^{3-} , F^- (d) Na^+ , Al^{3+}
- x. The third line in Balmer series corresponds to an electronic transfer between which Bohr's orbit in hydrogen.
 (a) $5 \rightarrow 3$ (b) $5 \rightarrow 2$ (c) $4 \rightarrow 3$ (d) $4 \rightarrow 2$.

2 Short questions and answers:

- i. How mass of electron can be calculated from e/m ratio and charge?
- ii. How does Mosley's Law help in the production of X-rays?
- iii. Which quantum number is also called sub-shell quantum number?
- iv. What is the difference between orbit and orbital?
- v. What is the relationship between?
 (a) energy and wavelength
 (b) frequency and wavelength
- vi. Which species are formed by the decay of neutron?
- vii. Hydrogen atom and He^+ are mono electronic system, but the size of He^+ is much smaller than H, why?
- viii. Why is 4s orbital lower in energy than 3d orbital?
- ix. Write electronic configuration of ${}_{25}Mn$, ${}_{30}Zn$, and ${}_{13}Al$.
- x. What is (n+l) rule?

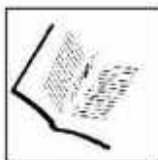


- xi. Point out the defects of Bohr's Model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle.
- xii. Calculate the energy of electron of a hydrogen atom in the orbit for which the value of $n = 3$. **Ans.** $E_3 = -145.92 \text{ kJ mole}^{-1}$
- xiii. Bohr's equation for the radius of n th orbit of electron in the hydrogen atom is

$$r_n = \frac{\epsilon_0 h^2 n^2}{\pi e^2 m}$$

- (a) When the electron moves from $n = 1$ to $n = 2$, how much does the radius change?
- (b) What is the distance travelled by the electron when it goes from $n = 8$ to $n = 3$?

Ans. (a) $1.587 \text{ \AA}$ (b) $29.095 \text{ \AA}$



3

THEORIES OF COVALENT BONDING AND SHAPES OF MOLECULES



After completing this lesson, you will be able to:

This is 12 days lesson
(period including homework)

- Describe the features of sigma and pi bonds.
- Describe the change in bond lengths of hetero-nuclear molecules due to difference in electronegativity values of bonded atoms.
- Describe the difference among molecular, network and metallic solids.
- Explain what is meant by the term ionic character of a covalent bond.
- Use VSEPR and VBT theories to describe the shapes of simple covalent molecules.
- Describe the shapes of some molecules using orbital hybridization.
- Predict the molecular polarity from the shapes of molecules.
- Determine the shapes of some molecules from the number of bonded pairs and lone pairs of electrons around the central atom.
- Define bond energies and explain how they can be used to compare bond strengths of different chemical bonds.
- Describe how knowledge of molecular polarity can be used to explain some physical and chemical properties of molecules.

INTRODUCTION

In this chapter we will discuss the shapes of molecules on the theoretical basis and some factors affecting their shapes and behaviours. We start by describing the VSEPR (valence shell electron pair repulsion) model, which allows us to connect two dimensional Lewis structures into three dimensional shapes.

You will see how molecular shape and bond polarity combine to create a polarity for the entire molecules and how molecular shape influences biological function. Then we consider two bonding theories based on quantum mechanics. Valence bond theory explains how the observed shape arises from the interactions of atomic orbitals. Molecular orbital theory proposes the existence of orbitals that extend over the whole molecule.

The Lewis concept of formation of covalent bond as a shared pair of electrons between two atoms does not explain shapes of molecules. Similarly, many other properties such as bond energy, relative strengths of bonds, and paramagnetism cannot be explained on the basis of this concept. However, modern theories of chemical bonding not only explain most of our experimental observations, but also allow us to predict the shapes and geometries of molecules. These theories can also be used to predict many physical and chemical properties of molecules.



3.1 SHAPES OF MOLECULES

The shapes of molecules can be predicted by Valence Shell electron pair repulsion (VSEPR) theory.

This theory was suggested by Sidgwick and Powell (1940). According to this theory, the shapes or geometry of a molecule or ion depends on the number of shared pairs as well as the lone pairs of electrons around the central atom of the molecule or ion.

Gillespie and Nyholm in 1957 proposed that the arrangement of atoms in a molecule is mainly determined by the repulsive interactions among all electron pairs in the valence shell of central atom.

Postulates of VSEPR Theory

The postulates of VSEPR theory are as follows:

1. The electron pairs present around the central polyvalent atom are arranged in space as far apart as possible so that, there is minimum repulsion between them.
2. A non-bonding pair or lone pair of electron occupies more space on the surface of an atom than a bonding pair.
3. Both the lone pairs as well as bond pairs determine the geometry of the molecules.
4. The magnitude of repulsion between the electron pairs in a given molecule decreases in the following order.

Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair

A Lone pair causes deviation from ideal bond angles, which in turn change regular geometry.

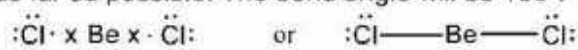
5. The two electron pairs of a double and three electron pairs of a triple bond contain a higher electron charge density. Therefore, they occupy more space than one electron pair of a single bond. However they behave like a single electron pair in determining the geometry of the molecules.

Applications of VSEPR Theory

The molecules and ions will be classified according to the number of electron pairs present in them, irrespective of the fact whether they are of bonding or nonbonding type. In order to illustrate this theory, consider hypothetical molecules having central atom "A" with more than one "B" type atoms bonded with it. Lone pair if present in the molecules is represented by "E".

(a) Shapes of molecules containing two electron pairs around a central atom. AB₂ Type

A molecule having two bond pairs of electrons but no lone pair around a central atom always has a linear geometry, because such an arrangement of atoms keeps the two pairs as far as possible. The bond angle will be 180°.



(b) Shapes of molecules containing three electron pairs around a central atom.

AB₃, AB₂E Type

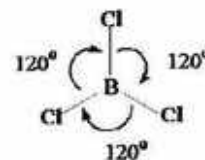
(i) AB₃ type with no lone pair

A molecule having three bond pairs of electrons but no lone pairs around a central atom always has a planar triangular geometry, because such an arrangement of atoms keeps the three pairs of electrons as far apart as possible. The bond angle will be 120°.

3. Theories of Covalent Bonding and Shapes of Molecules

Example: (BCl_3)

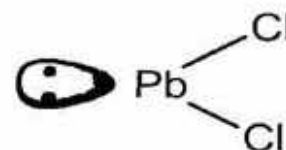
Boron trichloride (BCl_3) is a typical example of molecules, which contains three bond pairs of electrons. BCl_3 has trigonal planar shape. The bond angles will be 120° each. Other examples of this type are: AlH_3 , AlCl_3 , GaH_3 , InH_3 .



- (ii) AB_2E - type with one Lone pair and two bond pairs

Examples: PbCl_2 molecule
 SnCl_2 molecule

In case of PbCl_2 and SnCl_2 molecules, there are three electron pairs around the central atoms, one lone pair and two bond pairs. According to VSEPR concept the lone pair (non-bonding) of electron occupies more room and exerts a greater repulsion on the bond pairs resulting in the shortening of Cl-Pb-Cl angle. Thus, the shape of PbCl_2 molecule is distorted and becomes angular or V-shape with Cl-Pb-Cl bond angle less than 120° .

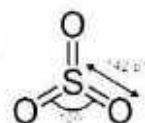


V. shaped PbCl_2 molecule

- (iii) AB_3 type with multiple bonds

Examples: SO_3

In SO_3 , all the three regions are occupied by S — O bonds. There is no lone pair hence the structure will be perfectly triangular having 120° .



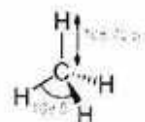
- (c) Shapes of molecules containing four electron pairs around a central atom AB_4 , AB_3E & AB_2E_2 Type.

- (i) AB_4 type with no lone pair

A molecule having four bond pairs of electrons but no lone pairs around a central atom always has regular tetrahedral geometry, because such an arrangement of atoms keeps the four pairs of electrons as far apart as possible. The bond angle will be 109.5° . The atoms are at the four corners of a regular tetrahedron.

Examples: CH_4 (Methane), CCl_4 , SiF_4 , SnCl_4 etc.

Methane is a typical example of this type.

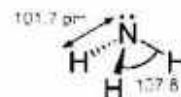


- (ii) AB_3E type with one lone pair and three bond pair

A molecule having three bond pairs and a lone pair around the central atom has triangular pyramidal geometry instead of tetrahedral. Due to repulsions between lone pair and bond pairs, the bond angles are reduced to 107.5° instead of 109.5° .

Example: NH_3 is a typical example.

Other examples: PH_3 , AsH_3 , SbH_3 , etc.



- (iii) AB_2E_2 type with two Lone pairs and two bond pairs

In this case, presence of two lone pairs, introduces three types of repulsions i.e. lone pair-lone pair, lone pair-bond pair and bond pair – bond pair.

Example: H_2O , H_2S etc.

VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pair in addition to bond pairs in determining overall geometry of water molecule. Two of the corners of a tetrahedron are occupied by each of the two lone pairs and remaining by bond pairs. But due to spatial arrangement of lone pairs and their repulsion among themselves and with the bond pairs, the bond angle is further reduced to 104.5° and geometry becomes V shaped.

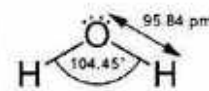
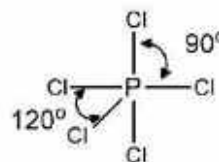


Table 3.1: Bonding and the shape of Molecules

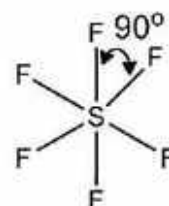
Table 3.1: Bonding and the shape of Molecules					
Number of Bond pairs	Number of Lone pairs	Total Number of Electron pairs	Molecular Shape	Examples	Ball-and-Stick Models
2	0	2	Linear	BeCl_2 , HgCl_2 , CO_2	 AB_2
3	0	3	Triangular	BF_3 , AlBr_3 , CH_2O	 AB_3
2	1	3	Bent	SO_2 , O_3	 AB_2E
4	0	4	Tetrahedral	CH_4 , CCl_4 , SiCl_4	 AB_4
3	1	4	Pyramidal	NH_3 , PCl_3	 AB_3E
2	2	4	Bent	H_2O , H_2S , SCl_2	 AB_2E_2
5	0	5	Trigonal bipyramid	PCl_5	 AB_5
6	0	6	Octahedral	SF_6	 AB_6

**(d) Molecules containing five electron pairs AB₅ – type**

With the increasing number of electron pairs, it becomes increasingly difficult to visualize the true shapes of the molecules. Thus a central atom containing five electron pairs presents a more complicated system. A trigonal bipyramid arrangement – represents a structure in which five electron pairs can have minimum repulsion. In PCl_5 , there are five electron pairs in the valence shell of phosphorus atom. All of them are bonding pairs and thus PCl_5 molecule adopts trigonal bipyramidal structure.

**(e) Molecules containing six electron pairs (AB₆ – type)**

Molecules, in which the central atom has six electron pairs, adopt octahedral geometry. The examples of such molecules are SF_6 , SeF_6 , TeF_6 .

**Prediction of shape of molecules:**

The following steps are generally required to predict geometrical shape by VSEPR-method.

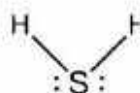
1. Draw dot diagram for the molecule.
2. Determine the number of valence electrons surrounding the central atom.
3. Determine the number of bond pairs and lone pairs of electrons.
4. Determine the geometrical distribution of electron pairs so that they are as far apart as possible.

Example:

Predict the shape of H_2S .

Solution:

Valence electrons of S-atom	=	6
Electrons contributed by 2H-atoms	=	2
Total no. of electrons around S-atom	=	8
Electron pairs	=	4
Bond pairs	=	2
Lone pairs	=	2



Thus H_2S is AB_2E_2 type molecule. It will possess V-shaped geometry

3.2 THEORIES OF COVALENT BONDING

There are two theories which are used to understand the nature of covalent bond.

- (i) The Valence bond theory (VBT)
- (ii) The Molecular orbital theory (MOT)

Valence bond theory (VBT)

This theory was proposed by Heitler and London (1927) and later on developed by Pauling. This concept is based on wave – mechanical treatment of molecules and has been successful in explaining the bond energies, bond lengths and shapes of covalent molecules.

According to valence bond theory, a covalent bond between two atoms is formed when the atoms come so close that a partially filled atomic orbital of one atom overlaps with a



partially filled atomic orbital of the other. The two overlapping atomic orbitals retain their identity. The term overlap means that the two orbitals share same common region in space.

Postulates of VBT:

1. A bond between two atoms is formed by the overlap of half filled atomic orbitals of two atoms. The two overlapping atomic orbitals retain their identity.
2. The two overlapping orbitals must have electrons of opposite spin.
3. The number of bonds formed by an atom is equal to the number of unpaired electrons present in the valence shell of the atom.
4. If only two orbitals overlap, a single bond is formed. If additional orbitals of atoms overlap then multiple bonds are formed.
5. In order to form a bond, the overlapping orbitals must have the same symmetry with respect to the bond axis.

"A line joining the nuclei of two bonded atoms is called bond axis"

6. In overlapping of orbitals energy is released. The greater the overlap between the orbitals, the greater is the energy released and the stronger will be the bond formed.

Types of overlapping and nature of covalent bonds

There are two main types of covalent bonds which are obtained by overlapping. These are:

- Sigma bond (σ)
- Pi Bond (π)

Sigma bond (σ)

"Any first bond formed between two partially filled atomic orbitals by head on overlap is called sigma bond"

In a sigma bond, the region of highest electron density is symmetrically distributed around the bond axis. The probability of finding the electron is maximum in the region between the two nuclei. The first bond formed between any two atoms is the sigma bond. All single covalent bonds are sigma bonds (σ) and the electrons occupying a bond are called σ electrons.

A sigma bond is formed by the overlapping of the following types as shown in figure 3.1.

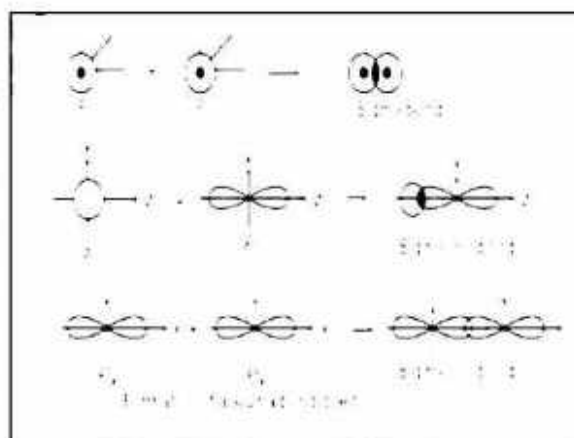


Figure 3.1: Formation of Sigma bonds

Pi (π) bond

"A bond formed between two already σ bonded atoms by the sidewise overlap of their two half filled p-atomic orbitals whose axes are parallel is called a Pi (π) bond."

In the formation of pi bond, the two overlapping p-orbitals must be coplanar and their axes must be parallel. The electron density in this bond is

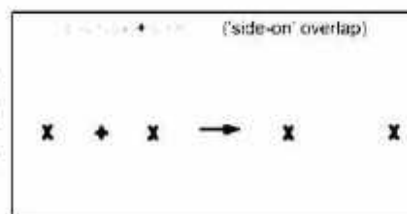


Figure 3.2: A Side wise view of overlap of $p_y - p_y$ orbitals in formation of π bond

unsymmetrical around the bond axis.

The probability of finding the electron is maximum in the region above and below the line joining the two nuclei. The overlap of p-orbitals in pi bond formation is not as good as in sigma bond. A pi bond is weaker than a sigma bond. One or two pi bonds can form between any two atoms already bonded covalently.

π bond is formed by side wise or lateral overlap between two p-orbitals which have their lobes perpendicular to the molecular axis. The side wise overlap is not too efficient, so result is a weak bond. **That's why sigma bond is always stronger than a pi bond.**

Remember:

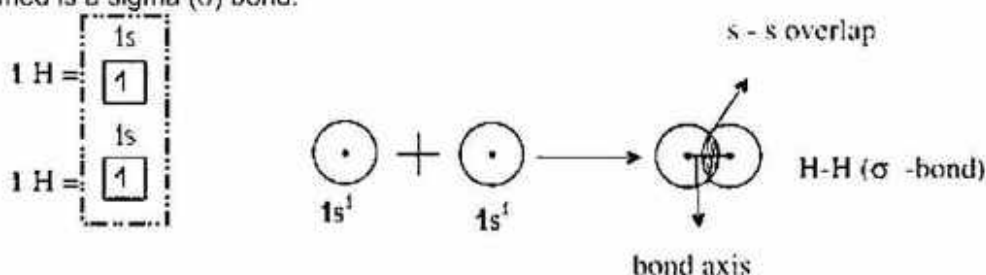
- In case of pi bond formation which is over a covalent bond, the electron density is greatest above and below the line joining the two nuclei and this is also called nodal plane.
- Only pure, parallel, co-planar, half filled p-orbitals on adjacent atoms can form a π bond.
- Only one bond in any multiple bonds can be a sigma bond, the remaining bonds are pi bonds.
- In case of hybridization, the overlapping of any hybrid-orbitals always produces a sigma (σ) bond.

Applications of Valence bond Theory

Single Bond Formation

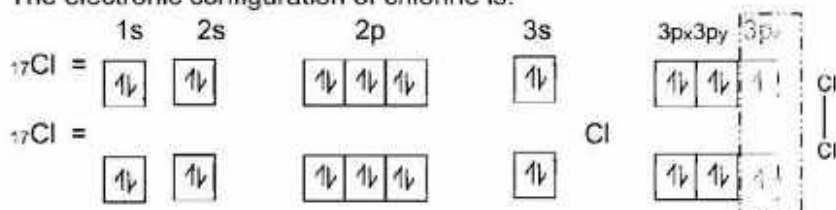
a) Formation of H_2 molecule

Each H atom has the electron configuration $1s^1$. As two hydrogen atoms approach each other, their half filled 1s orbitals overlap, giving H-H bond. The overlap of orbitals provides a means for sharing electrons, thereby allowing each 1s to complete its valence shell. The electron density is concentrated in the region along the line joining the two nuclei. The bond formed is a sigma (σ) bond.



b) Formation of Cl_2 molecule

The electronic configuration of chlorine is:



Each Chlorine atom has one half-filled $3p_z$ orbitals. On the basis of VBT, sigma bond is formed between two Cl atoms by head on overlap of half-filled $3p_z$ atomic orbital of each chlorine atom.

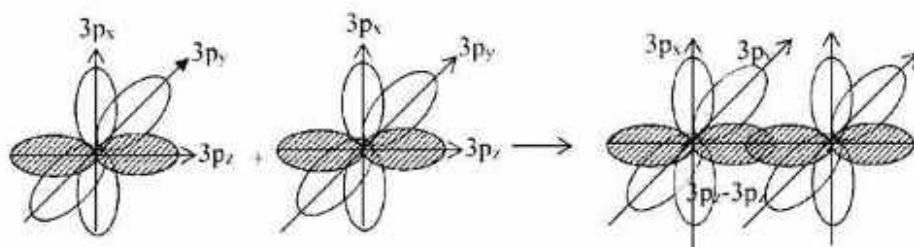


Figure 3.4: Orbital diagram of Cl₂

c) Formation of HF molecule

The electronic configurations of F and H atoms are:

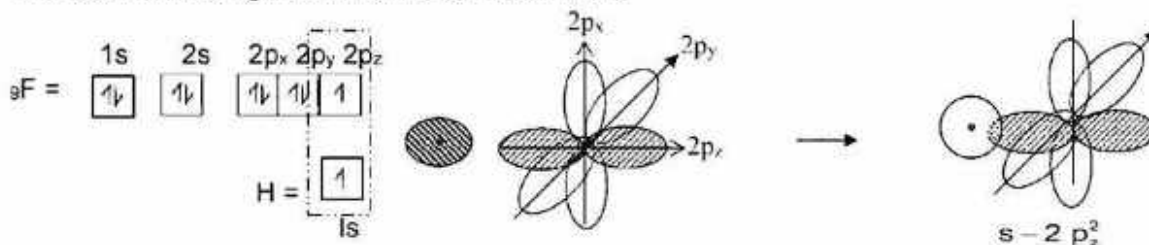


Figure 3.5: Orbital diagram of HF

In the formation of HF molecule, the half-filled 1s orbital of H atom overlaps with the half-filled 2p_z orbital of F to form σ bond.

Multiple bond formation

a) Formation of O₂ molecule

Oxygen molecule, O₂ is obtained by the combination of two oxygen atoms. Electronic configuration of an oxygen atom is:

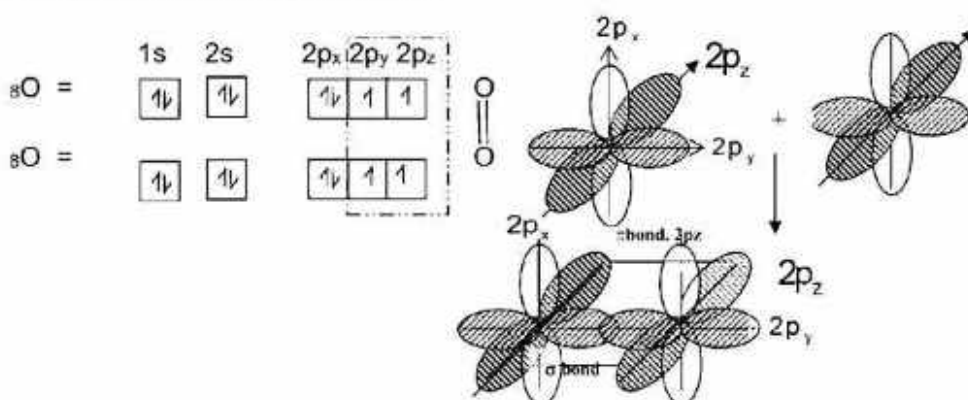


Figure 3.6: Orbital diagram of O₂



Each oxygen atom has two half-filled $2p$ orbitals in the valence shell. On the basis of VBT two covalent bonds can be formed between two O atoms. One bond is formed by the end-to-end overlap of half-filled $2p_x$ orbitals on each oxygen atom. This gives a σ bond. The second bond is formed by the side-to-side overlap of half-filled $2p_y$ orbitals on each oxygen atom. This gives a π bond. Thus a double bond is formed between two oxygen atoms. One is σ bond while the other is π -bond.

b) Formation of N_2 molecule:

Nitrogen molecule, N_2 is formed by the combination of two N atoms. The electronic configuration of N atom is:

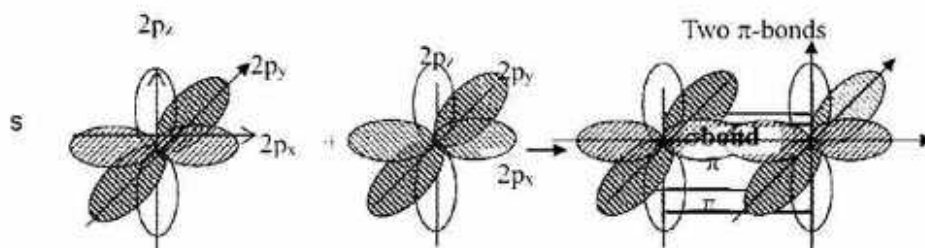
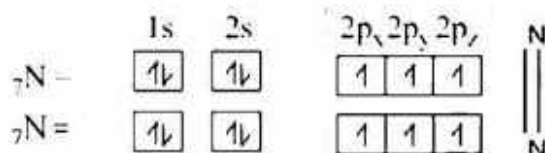


Figure 3.7: Orbital diagram of N_2

Each N atom has three half-filled p orbitals. On the basis of VBT, three covalent bonds can be formed between two nitrogen atoms. When the two nitrogen atoms approach each other, their $2p_x$ orbitals undergo end-to-end overlap, giving a σ bond. The end-to-end overlapping brings the two nitrogen atoms so close together that their parallel $2p$ orbitals undergo side-to-side overlap to produce two π bonds. Note that each π bond is in two separate regions surrounding a σ bond. There are five distinct regions of electron charge density in the nitrogen molecule.

- The σ electrons between the nuclei forming a σ bond.
- The π electrons above and below the σ electrons forming a π bond.
- The π electrons in front of and behind the σ electrons forming another π bond.

Thus a triple bond is formed between two nitrogen atoms; one is σ bond while the other two are π bonds.

Hybridization of Atomic Orbitals

Valence number shown by any element generally corresponds to the number of partially filled (half-filled) orbitals in an atom of that element. However this is not always the case because if only the unpaired electrons in an atom were permitted to form bond, e.g. beryllium

whose electronic configuration is $1s^2 2s^2$ would be inert. Boron which has the electronic structure $1s^2 2s^2 2p_x^1$ would have a valency of one and carbon (${}_6\text{C}$) with the electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1$ would show a valency of two. In actual practice, beryllium shows a valency of two, boron has a valency of three and carbon has a valency of four.

Pauling and Slater resolved this discrepancy by introducing the concept of orbital hybridization which involves mixing of the pure s and p (one or more) orbitals of an atom to form new hybrid orbitals, before the bonding process takes place. The number of hybridized orbitals are equal to the number of atomic orbitals overlapped. A bonding process can then be considered as a process of overlapping the hybrid atomic orbital of one atom with a pure or hybrid atomic orbital of another.

As we know simple valence Bond theory does not explain the covalent bond formation of certain elements. So modification in this theory was made in the form of "hybridization concept".

So a process of mixing atomic orbitals of different energy and shape to form set of new orbitals of the same energy and same shape is called hybridization and the orbitals so obtained are called "hybrid orbitals". According to this concept atomic orbitals differing slightly in energy intermix to form new orbitals of equal energies and are called hybrid orbitals which differ from the parent atomic orbitals in shape and energy and possess specific geometry. It also gives a satisfactory explanation for the valency of the elements. In this process, the electron belonging to the ground state structure are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.

The atomic orbitals, undergo hybridization. The energy required for the excitation is compensated by the energy released during the process of bond formation with other atoms. Depending upon the nature of orbitals involved there are many types of hybridization.

For example, sp^3 , sp^2 , sp hybridization

(i) sp^3 Hybridization

"The process of mixing one's orbital and three p orbitals to form four new equivalent sp^3 hybrid orbitals is called sp^3 hybridization"

Let us discuss the structure of methane, ammonia and water by understanding the sp^3 hybridization of carbon, nitrogen and oxygen atoms.

a) Structure of Methane

$${}_6\text{C} \text{ (Ground state)} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$$

$${}_6\text{C}^* \text{ (Excited state)} = 1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$$

$${}_6\text{C} \text{ (Hybrid state)} = 1s^2, (sp^3)^1, (sp^3)^1, (sp^3)^1, (sp^3)^1$$

When carbon atom in a molecule is attached to four other atoms, then sp^3 hybridization occurs.

Each sp^3 hybrid orbital consist of two lobes, one larger and the other smaller. The energies of hybrid orbitals

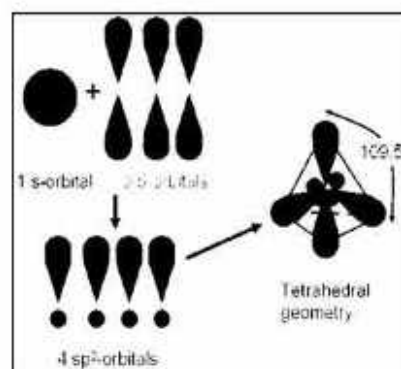


Figure 3.8: Structure of sp^3 hybridized orbitals

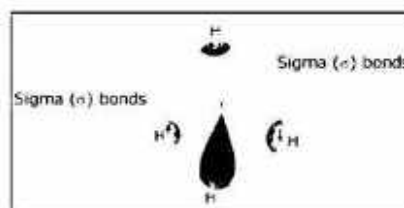


Figure 3.9: Structure of Methane (CH_4)

Methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with $1s$ orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule of methane, thus formed possesses a tetrahedral geometry. The C-H bonds which result from sp^3 - s overlaps are directed towards the corners of a regular tetrahedron. Each H-C-H bond angle is 109.5° . The tetrahedral structure of CH_4 molecule has four faces and four corners.

In NH_3 molecule, the central atom is nitrogen. It contains five electrons in its valence shell.

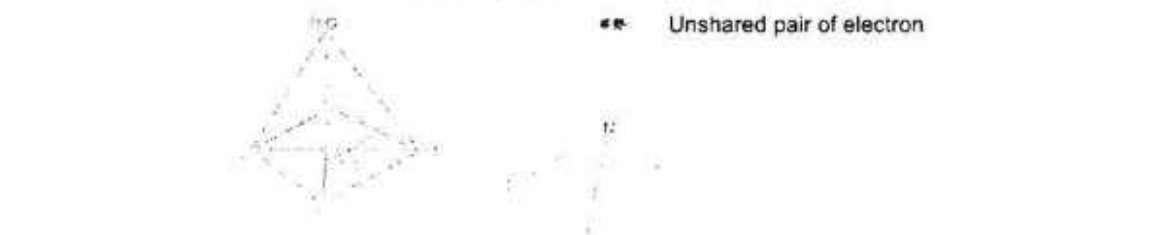
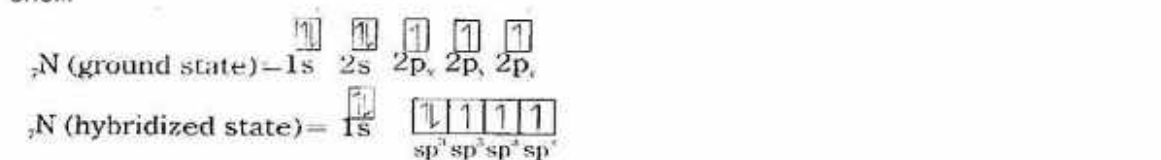
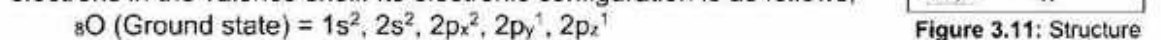


Figure 3.10: Structure of Ammonia (NH_3)

Hence one s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals. They are directed towards the four corners of a tetrahedron. One of the hybrid orbitals is completely filled by a lone pair of electrons and the remaining three orbitals are half filled. The half filled sp^3 hybridized orbitals of nitrogen overlap with three 1s-orbitals of hydrogen atoms. The three hydrogen atoms are located at three corners, whereas the lone pair of electron is at the fourth corner of the tetrahedron. This results in a **pyramidal** molecule, in which three hydrogen atoms form the base and the lone pair of electrons the apex as shown in the fig 3.10. The experimentally determined value of H-N-H bond angle in NH_3 molecule is **107.5°** which is less than the normal tetrahedral value of 109.5° . The deviation from the tetrahedral angle is explained on the basis of repulsion between lone pair and bond pairs. The lone pair-bond pair repulsion is greater than bond pair-bond pair repulsion. As a result, the bond pairs move away from the lone pair and come closer to each other. Hence, the angle between bond pairs decreases.

c) Structure of Water H_2O

In H_2O molecule, the central atom is oxygen. It contains six electrons in the valence shell. Its electronic configuration is as follows,





$\text{sO (Hybrid state)} = 1\text{s}^2, (\text{sp}^3)^2, (\text{sp}^3)^2, (\text{sp}^3)^1, (\text{sp}^3)^1$

One 2s and three 2p orbitals of O-atom intermix to produce four sp^3 hybrid orbitals. The four sp^3 hybrid orbitals are directed towards the four corners of a regular tetrahedron with oxygen atom at the centre. Two of the sp^3 hybrid orbitals contain two lone pairs of electrons, each and are completely filled. The remaining two sp^3 hybrid orbitals contain one electron each and are partially filled. Thus the two partially filled sp^3 hybrid orbitals now overlap with the two 1s orbitals of two hydrogen atoms to form two sigma bonds. Each sigma bond is formed by sp^3 -s overlap. The two hydrogen atoms are located at two corners of a tetrahedron, whereas the two lone pairs at the remaining two corners of the tetrahedron. The result is a **V-shaped** molecule. The experimentally determined value of H-O-H bond angle in H_2O molecule is 104.5° , which is lesser than the normal tetrahedral value (109.5°). The deviation from the tetrahedral angle is explained on the basis of repulsion between lone pairs and bond pairs. The repulsion of lone pair-lone pair > lone pair-bond pair > bond pair-bond pair. As a result, the bond pairs move away from the lone pairs and come closer to each other. Hence the angle between bond pairs decreases up to 104.5° .

(iii) sp^2 - Hybridization

"The mixing of one s and two p orbitals of the same atom to form three identical sp^2 hybrid orbitals is called sp^2 -hybridization"

The hybrid orbitals are directed towards the three corners of an **equilateral triangle**. The angle between any two hybrid orbitals is 120° . Each sp^2 hybrid orbital has 33.3% s-character and 66.7% p-character. The sp^2 hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.

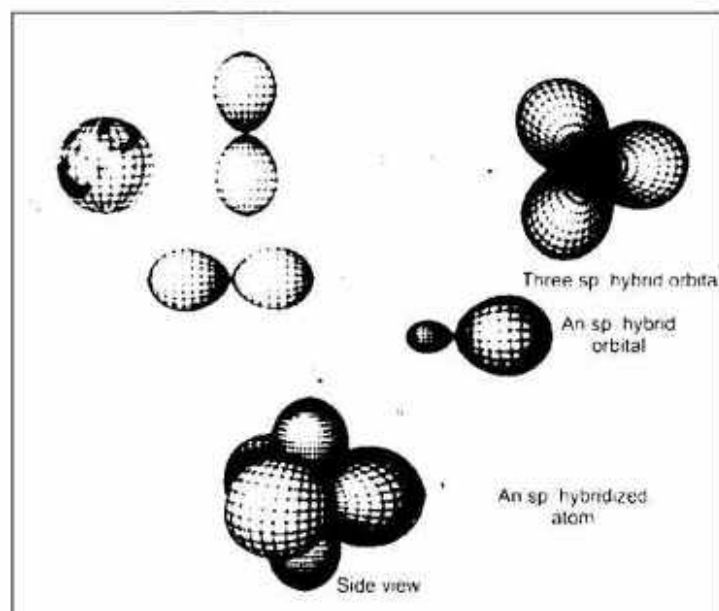


Figure 3.12: Structure of Hybridization (sp^2)

Examples: Boron trifluoride and Ethene

a) Structure of Boron trifluoride, BF_3

In BF_3 molecule, the central atom is boron. It contains three electrons in its valence shell. The electronic configuration of the valence shell of B-atom in the ground and excited states are as follow,

$${}_5\text{B} = 1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0 \text{ (ground state)}$$

$${}_5\text{B} = 1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^0 \text{ (excited state)}$$

One 2s and two 2p orbitals of boron atom intermix to give three sp^2 hybridized orbitals. The three sp^2 hybrid orbitals lie in the same plane and are directed towards the corners of an equilateral triangle with boron atom at the centre.

Thus the angle between any two sp^2 orbitals is 120° . The three sp^2 orbitals contain one electron in each and are thus partially filled. The partially filled 2p orbitals of three fluorine atoms overlap with each sp^2 hybrid orbitals of boron atom to form three sp^2-p_z sigma bonds. As a result, BF_3 molecule has **triangular planar** structure.

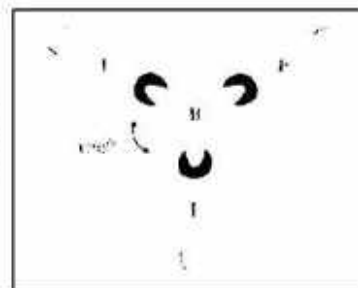


Figure 3.13: Structure of BF_3

b) Structure of Ethene, $\text{CH}_2 = \text{CH}_2$

the electronic configuration of carbon atom is:

$${}_6\text{C} \text{ (Ground state)} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$$

$${}_6\text{C} \text{ (Excited state)} = 1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$$

$${}_6\text{C} \text{ (Hybrid state)} = 1s^2, (sp^2)^1, (sp^2)^1, (sp^2)^1, 2p_z^1$$

In $\text{CH}_2 = \text{CH}_2$ molecule, one s and two p orbitals of each C-atom intermix to form three hybrid sp^2 orbitals. The geometry of molecules depends upon the orientation of hybrid orbitals. Hybrid orbitals are **triangular planar** and oriented at the angle of 120° to each.

Each atom is left with one half filled p-orbital perpendicular to the planar sp^2 hybrid orbitals. One sp^2 orbital of each C-atom overlaps linearly to form one C-C sigma bond. Remaining two sp^2 orbitals of each C-atom overlap linearly with 1s atomic orbital of H-atom to form two C-H single bonds.

A pi-bond is formed by the sideways overlap of two half-filled co-planar p-orbitals in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei.

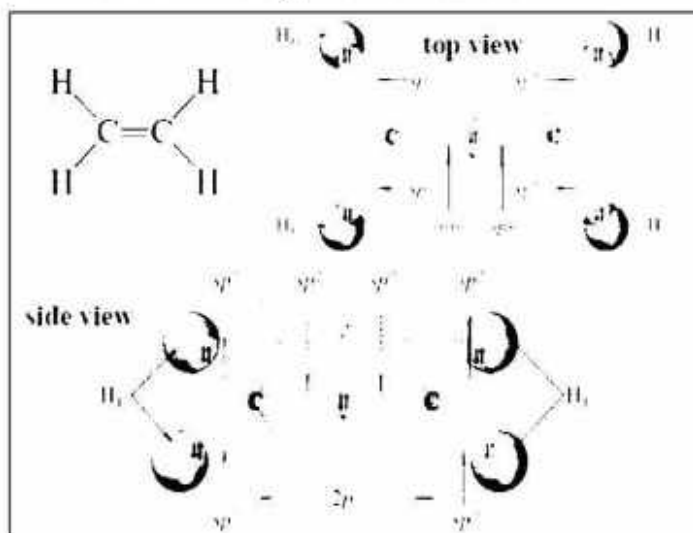


Figure 3.14: Structure of Ethene

(iii) sp - Hybridization

"The mixing of one s-orbital and one p-orbital of an atom to form two equal energy hybrid orbitals is called sp hybridization"

The two sp hybrid orbitals are **linear** and angle between them is **180°** . Each sp -hybrid orbital has 50% s-character and 50% p-character. The sp -hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.

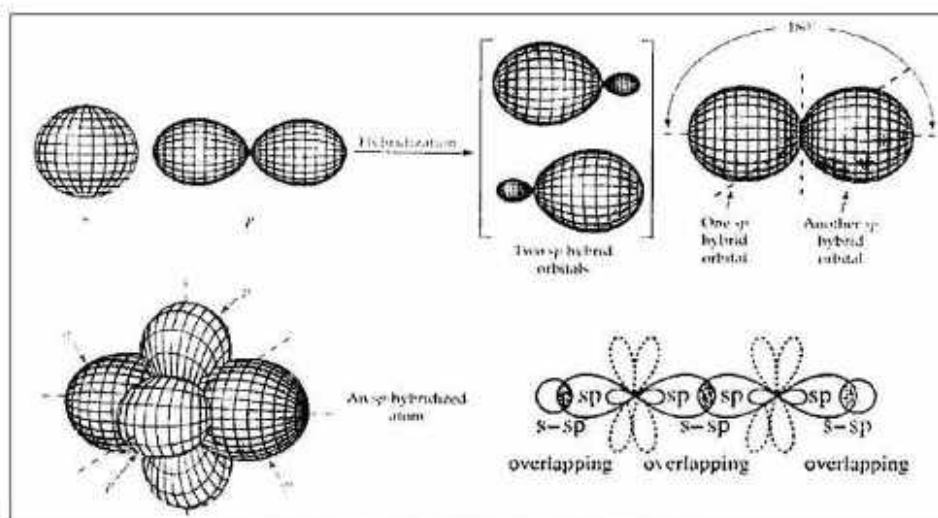
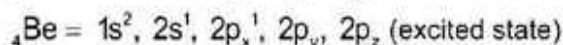
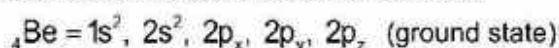


Figure 3.15: Structure of sp Hybridized orbitals

Examples:- BeCl_2 , C_2H_2

a) Structure of BeCl_2 [Beryllium Chloride]

In BeCl_2 molecule, the central atom is beryllium atom. Beryllium atom contains two electrons in its valence shell. The electronic configuration of valence shell of beryllium atom in the ground state and excited state is as follow:



One 2s and one 2p orbitals of beryllium atom intermix to form two sp hybrid orbitals. Each sp hybrid orbital contains one electron. The two sp hybrid orbital lie in a straight line with beryllium atom at the centre. One sp orbital of Be overlaps linearly with p-orbital of other Cl to form Be-Cl sigma bond remaining sp hybrid orbital of Be overlaps linearly with $3p_z$ orbital of second Cl atom to form sigma bond. Thus BeCl_2 molecule is **linear**. The Cl-Be-Cl bond angle is **180°** .

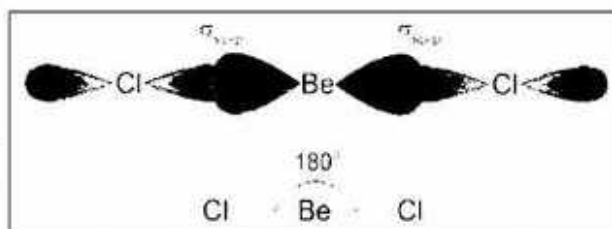


Figure 3.16: Structure of beryllium chloride

b) Structure of Ethyne, $\text{CH} \equiv \text{CH}$

The electronic configuration of carbon atom in the ground and excited states is as follow:

$${}_6\text{C} \text{ (Ground state)} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$$

$${}_6\text{C} \text{ (Excited state)} = 1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$$

$${}_6\text{C} \text{ (Hybrid state)} = 1s^2, (sp)^1 (sp)^1, 2p_y^1, 2p_z^1$$

One 2s and one 2p orbitals of carbon atom intermix to give two sp hybrid orbitals. The $2p_y$ and $2p_z$ orbitals remain unhybridized. Each sp hybrid orbitals contains one electron. The two sp hybrid orbitals are directed along a straight line at an angle of 180° between them. The two unhybridized p orbitals which are perpendicular to each other are also perpendicular to the plane of the two sp hybrid orbitals. Thus each carbon atom possesses two sp hybrid orbitals and two pure p atomic orbitals. Each C-atom undergoes sp-s overlap with one H-atoms and sp-sp overlap with other carbon atom to form two σ -bonds.

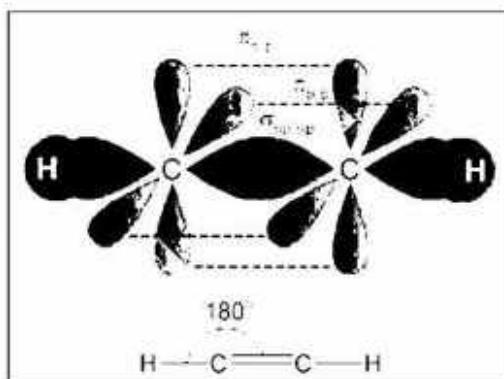


Fig. 3.17: Structure of ethyne molecule

The two half-filled p orbitals of two carbon atoms overlap sideways to form two π -bonds. Thus ethyne molecule contains one σ -bond and two π -bonds between two carbon atoms and two carbon-hydrogen σ -bonds. The electronic clouds of two π -bonds merge into each other to form cylindrical shaped π -electron cloud. The molecule is **linear** in shape.

Drawbacks of Valence Bond Theory

It fails to explain:

- The formation of coordinate covalent bond.
- The formation of odd electron molecules or ions.
- The paramagnetic behaviour of oxygen molecule.

The method of molecular orbital theory was developed in 1927-1928 by Hurd and Mullikan and in 1929 by Lennard-Jones.

It is assumed that linear combination of atomic orbitals form new orbitals called molecular orbitals which are characteristics of the whole molecule. The molecular orbital surrounds two or more nuclei of the bonded atoms. Two atomic orbitals after combining linearly form two molecular orbitals which differ in energy. One of them, having lower energy, is called **bonding molecular orbital (BMO)** while the other having high energy is called **anti-bonding molecular orbital (ABMO)**. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital, while the anti-bonding molecular orbital is designated as σ^* .



The filling of electrons into the molecular orbitals takes place according to

- Aufbau principle
- Pauli's exclusion principle
- Hund's Rule

The two electrons from each atom fill the low energy σ orbital or π orbital while the high energy σ^* orbital or π^* orbital may have electrons or remain empty.

The following diagram illustrates the formation of the molecular orbitals (lower energy and higher energy) and also the processing of filling of electrons according to the rules mentioned above.

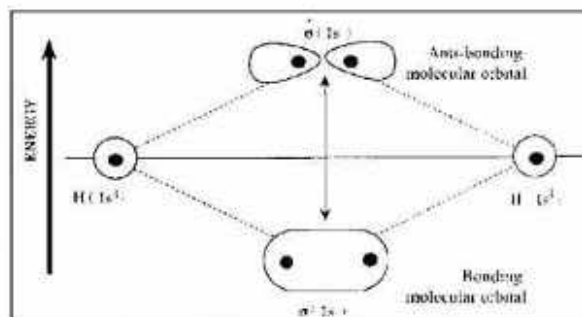


Figure 3.18: Energy diagram of bonding and anti-bonding molecular orbitals

In this type of diagram, the combining atomic orbitals are shown on two extremes and the resulting molecular orbitals (MO) are represented in the middle column.

Atomic orbitals of same energy are shown at the same level. The difference between the energies of atomic orbitals and the bonding MO's depend upon the extent of overlap of atomic orbitals. A large overlap results in greater lowering of the energy of bonding MO (and a corresponding large rise in energy in the anti-bonding MO). Larger the overlap, stronger will be the resulting bond. According to the above diagram, the sequence of energy levels in which they are filled up is,

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$$

There are two types of overlapping in molecular orbital theory

- Head on approach (linear overlapping) or linear combination
- Sideways approach (parallel overlapping)

i. Head on approach (linear overlapping)

Head on approach can take place between s-s, s-p and p-p atomic orbitals.

When two s atomic orbitals overlap, they form two molecular orbitals. Molecular orbital having low energy than atomic orbital is called σ s. Molecular orbital which has high energy than atomic orbital is called σ^* s orbital as shown in the figure 3.18.

ii. Sideways approach or parallel overlapping

When the axes of two-p orbitals (i.e. p_y or p_z orbitals) are parallel to each other, they interact to form molecular orbitals.

The bonding molecular orbital $\pi(2p_y)$ or $\pi(2p_z)$ has zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane. On the other hand, $\pi^*(2p_y)$ or $\pi^*(2p_z)$ anti-bonding molecular orbital has the least electron density in the inter-nuclear region. Since the $2p_y$ and $2p_z$ atomic orbitals are degenerate orbitals (having the same energy) the π molecular orbitals i.e., $\pi(2p_y)$ and $\pi(2p_z)$ are also degenerate. Similarly the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ molecular orbitals are also degenerate.

Two sets of 2-p atomic orbitals form six molecular orbitals (three bonding and three anti-bonding). The bond formed as a result of linear overlapping is σ bond while that formed as a result of sideways overlap is called a π (pi) bond. Thus p orbital overlaps can lead to the



formation of three bonds. One sigma and two pi bonds.

Bond order (No. of bonds)

The number of bonds formed between two atoms after the atomic orbitals overlap is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No. of electrons in BMOs} - \text{No. of electrons in ABMOs}}{2}$$

The number of bonds formed in hydrogen molecule may be calculated as follows.

$$\begin{aligned} \text{No. of electrons in the bonding orbitals} &= 2 \\ \text{No. of electrons in the anti-bonding orbitals} &= 0 \\ \text{Bond order} &= \frac{2-0}{2} = 1 \end{aligned}$$

It is a common practice that only MOs formed from valence orbital are considered in bond order calculations. It should be noted that a bond between two atoms can be formed only, when the number of electrons in the bonding orbital must be greater than the number of electrons in the anti-bonding molecular orbitals.

Relative Energies of the Molecular Orbitals

The relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals are determined by spectroscopic measurements.

a) The molecular orbitals of diatomic molecules such as O_2 , F_2 and their positive and negative ions can be shown in the following increasing order of energy.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_x) < \pi(2p_y) = \pi(2p_z) < \pi^*(2p_y) = \pi^*(2p_z) < \sigma^*(2p_x)$$

b) The diatomic molecule such as H_2 , He_2 , B_2 , C_2 , and N_2 (lighter molecules) show slightly different energy order.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_y) = \pi(2p_z) < \sigma(2p_x) < \pi^*(2p_y) = \pi^*(2p_z) < \sigma^*(2p_x)$$

Reason

We have seen in the energy order of lighter molecules like B_2 , C_2 , N_2 , $\sigma 2p_x$ is higher in energy than $\pi 2p_y = \pi 2p_z$ molecular orbitals. This reversal is due to mixing of 2s and $2p_x$ atomic orbitals.

Actually, the energy difference of 2s and 2p atomic orbitals is small; there is a possibility of mixing of these orbitals (hybridization of A.O.). As a result $\sigma 2s$ and $\sigma^* 2s$ MO do not retain pure s-character.

Similarly, $\sigma 2p_x$ and $\sigma^* 2p_x$ MOs do not have pure p-character. All the four MOs acquire sp-character. Due to this mixing, their energies change in such a way that MOs $\sigma 2s$ and $\sigma^* 2s$ become more stable and are lowered in energy MOs as $\sigma 2p_x$ and $\sigma^* 2p_x$ become less stable and are raised in energy. Since, $\pi 2p_y = \pi 2p_z$ remains unchanged. $\sigma 2p_x$ is raised to such an extent that it becomes higher in energy than $\pi 2p_y$ and $\pi 2p_z$.

But, O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 kJ/mol and 2078 kJ/mole for O_2 and F_2 respectively. The values are 554 kJ/mol for Boron, 846 kJ/mol for carbon and 1195 kJ/mol for nitrogen and these energy differences have been calculated by spectroscopic techniques.

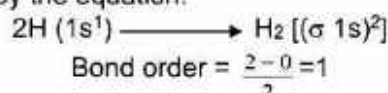
Applications of Molecular Orbital Theory for Homo Nuclear Diatomic Molecules

After having discussed the basic principles of molecular orbital theory, we are now able to take up the electronic structures and bonding properties of some homo-nuclear molecules.

(1). Hydrogen Molecule (H_2)



Hydrogen molecule is formed from the overlap of 1s atomic orbitals of two hydrogen atoms. They give rise to two molecular orbitals $\sigma 1s$ and $\sigma^* 1s$. The molecule has two electrons which occupy the lower energy $\sigma 1s$ orbital as shown in the diagram. The electronic configuration of the molecule is represented by the equation.



Thus the two hydrogen atoms are bonded through only one bond in the molecule. We conclude that the H_2 molecule is stable. It has bond dissociation energy of 436 KJmol^{-1} and is diamagnetic in nature i.e. (atoms, ions or molecules in which electrons are all paired in their molecular electronic configuration are diamagnetic). They are repelled by both poles of magnet.

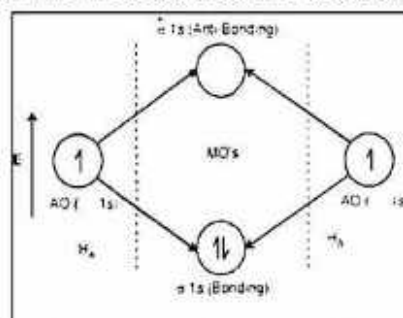
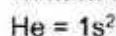


Figure 3.19: Molecular orbitals energy level diagram of H_2

(2). Helium Molecule (Hypothetical) He_2



The energy level diagram for He_2 is similar to that of H_2 except that it has two more electrons which occupy the anti-bonding $\sigma^* 1s$ orbital shown in the diagram.

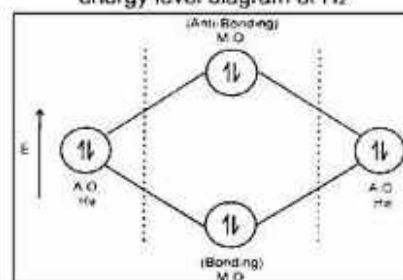
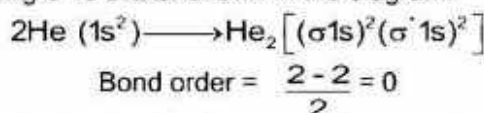


Figure 3.20: Molecular orbitals energy level diagram of He_2

Thus its bond order is zero and we conclude that the molecule is not stable. Infact, He_2 is not known, helium exist only as mono-atomic molecules.

(3). Lithium Molecule (Li_2)



The electronic configuration for Li_2 has a total of six electrons, two each in $\sigma 1s$, $\sigma^* 1s$ and $\sigma 2s$ molecular orbitals. In short hand notation this can be represented as $\sigma 1s^2$, $\sigma^* 1s^2$ and $\sigma 2s^2$. There are two more electrons in the bonding orbitals than in anti-bonding orbitals and the bond order is one. We conclude that the molecule is stable and diamagnetic it is indeed to exist in the vapour phase. It possesses bond energy of 110 kJ mol^{-1} which is less than H_2 molecule.

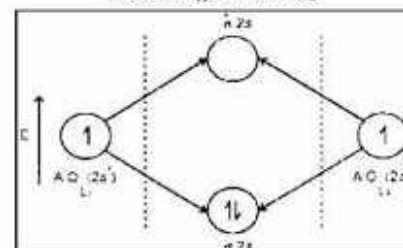
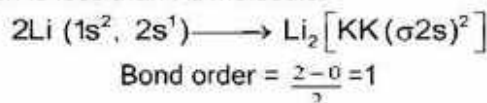


Figure 3.21: Molecular orbitals energy level diagram of Li_2

(4) Beryllium Molecule Be_2 

The situation for the Be_2 molecule is similar to that for He . Bonding and anti-bonding orbitals are equally populated and the bond order is zero. The electronic configuration is $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$. The Be_2 molecule is known but is very unstable.

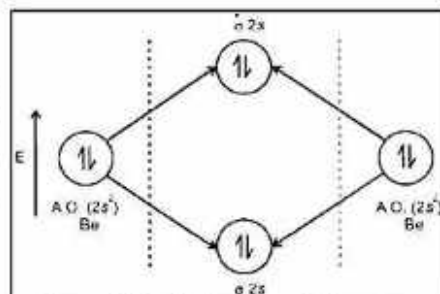
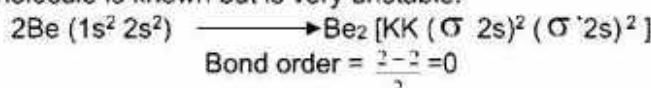
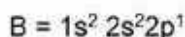


Figure 3.22: Molecular orbitals energy level diagram of Be_2

(5) Boron Molecule, B_2 

The boron atom has the configuration of $1s^2, 2s^2, 2p^1$ and is the first element with five electrons to participate in bonding.

Spectroscopic study has suggested that for B_2 , C_2 and N_2 molecules $\pi 2p$ orbitals are lower in energy than $\sigma 2p$ orbital. Thus the electronic configuration of B_2 is:

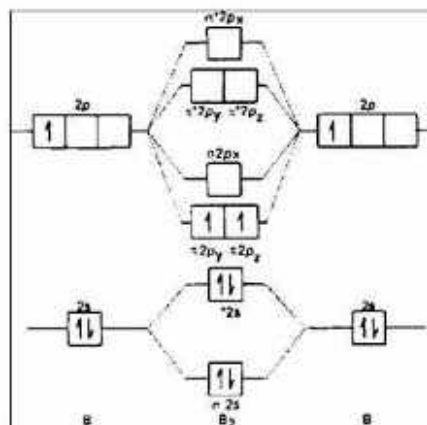
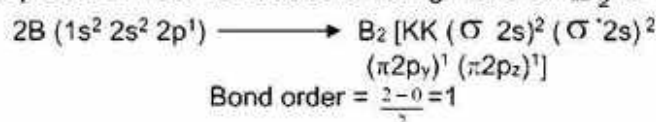
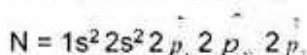


Figure 3.23: Molecular orbitals energy level diagram of B_2

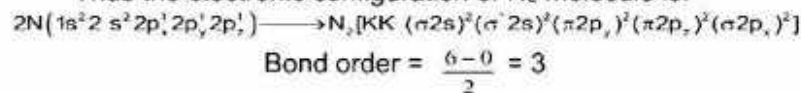
Thus the two B-atoms are bonded through only one bond in the molecule. The experiments verify not only that the molecule exists in vapour phase but that it is paramagnetic (atoms, ions or molecules) with two unpaired electrons. The bond energy is 270 kJ mol^{-1} .

Molecules which have one or more unpaired electrons in their molecular electronic configuration are paramagnetic. They are attracted to magnetic field.

(6) Nitrogen Molecule N_2 

Looking at, the electronic configuration, only $2s$ and three $2p$ electrons from each N atom are to be considered in the bond formation.

Thus the electronic configuration of N_2 molecule is:



It is obvious that the two N-atoms are bonded through triple bond. N_2 molecule is very stable molecule and has a very high bond energy 946 kJ mol^{-1} , which is consistent with MOT. It is diamagnetic in nature and possesses a very short bond length.

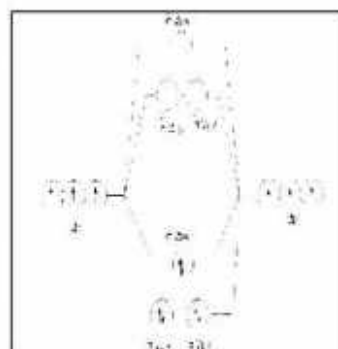
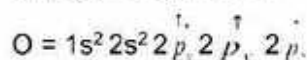


Figure 3.24: Molecular orbitals energy level diagram of N_2

(7) Oxygen Molecule O_2



The valence bond theory predicts that O_2 would be diamagnetic. However experiments show that it is paramagnetic having two unpaired electrons. A structure consistent with this observation is predicted by MOT. Spectroscopic evidence indicates that for O_2 , the σ_{2p} orbital is lower in energy than π_{2p} orbitals. The electronic configuration of O_2 molecule is:

$$2O(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1) \longrightarrow O_2[KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi_{2p_y}^*)^1(\pi_{2p_z}^*)^1]$$

$$\text{Bond Order} = \frac{6 - 2}{2} = 2$$

It is obvious that the two oxygen atoms are bonded through a double bond. The two unpaired electrons reside in the degenerate anti-bonding orbitals $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$, hence it is paramagnetic in nature. So we conclude that the molecule should be very stable as it possesses high bond energy i.e. 498 kJ mol^{-1} with bond length $1.21 \text{ \AA}$.

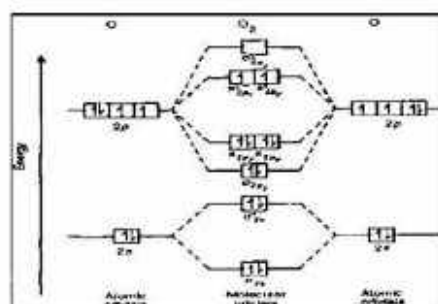
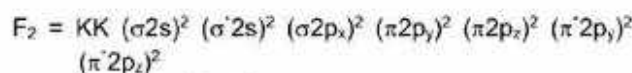


Figure 3.25: Molecular orbitals energy level diagram of O_2

(8) Fluorine Molecule F_2



Each F-atom has the $1s^2 2s^2 2p^5$ configuration. The participating electronic configuration of F_2 molecule is:



$$\text{Bond Order} = \frac{6 - 4}{2} = 1$$

It is obvious that two F-atoms are bonded through a single bond. The F-F bond distance is longer ($1.43 \text{ \AA}$) than the bond distance for O_2 ($1.21 \text{ \AA}$) and N_2 ($1.09 \text{ \AA}$) molecules. The bond energy of F_2 molecule is quite low (159 kJ mol^{-1}). It is diamagnetic in nature.

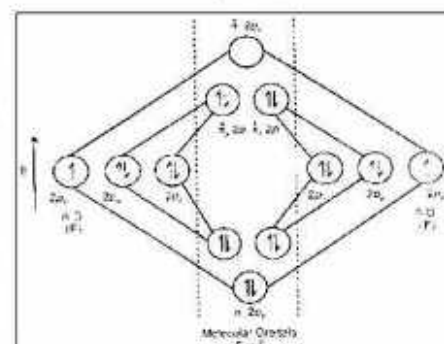


Figure 3.26: Molecular orbitals energy level diagram of F_2

Comparison of Valence Bond and Molecular Orbital Theories:

Similarities:

The common features of the two theories are:

- Both the theories explain the formation of covalent bond.
- In both the theories, a covalent bond is formed by the overlapping of atomic orbitals having appropriate symmetry about the molecular axis.
- According to both, the electronic charge resides in the region between the atomic nuclei.
- Both the methods lead to the formation of two types of bonds σ and π bonds.
- In both the methods, the atomic and molecular orbitals are filled up according to the same principles.



Differences:

Valence Bond Theory	Molecular Orbital Theory
1. According to this theory only valence electrons are involved in bond formation	1. According to this theory, all the electrons of interacting atoms are involved in bond formation
2. In VBT the two concerned atomic orbitals do not lose their individual identity	2. In MOT, the two atomic orbitals lose their individual identity
3. It does not explain the paramagnetic behaviour of molecules like O_2 molecule	3. It explains the paramagnetic behaviour i.e., electrical properties.
4. It does not give idea about the bond order	4. It gives idea about bond order by which we can determine that whether the bond is single, double or triple
5. It does not explain the non-existence of He_2 molecule.	5. It explains the non-existence of He_2 molecule.

3.3 BOND ENERGY (BOND ENTHALPY)

When a bond is formed between two atoms, energy is released (exothermic process), the same amount of energy is absorbed (endothermic process) when the bond is broken to form neutral atoms. So the **bond energy is the amount of energy required to break all bonds of particular type in one mole of the substance**. The strength of a bond is measured by its bond energy. The higher the bond energy, the stronger is the bond. It is determined experimentally by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is a measure of enthalpy change at 298K. **The enthalpy change in splitting a molecule into its component atoms is called enthalpy of atomization.**

Units

It is expressed in kilojoules per mole (kJ mol^{-1}). It is the energy required to break up an Avogadro number (6.02×10^{23}) of bonds i.e. one mole of bond. It is found that energies of multiple bonds are greater than those of single bonds. But a double bond is not twice as strong as a single bond or a triple bond is not thrice as strong as a single bond. It means that a σ bond is stronger than a π bond. Also, a polar covalent bond is stronger than a non-polar covalent bond.

Examples

- The bond energy of H-H in H_2 molecule at 25°C (298K) is 436 kJ/mole . The bond energy of Cl-Cl bond in Cl_2 molecule at 25°C is 242 kJ/mole .
- The bond energy of H-Cl bond in HCl molecule at 25°C is 431 kJ/mole .

Ionic character and Bond energy:

Bond energy is a measure of bond strength. Higher the bond energy, the stronger is the bond. The strength of a bond depends upon the following factors.

- Electronegativity
- Size of the bonded atoms
- Bond length
- Bond order (number of bonds)



“Greater the difference in electronegativity between the bonded atoms, the greater is the bond energy and stronger is the bond”

Examples

Bond type H-X	H-F	H-Cl	H-Br	H-I
Bond energy (kJmol ⁻¹)	567	431	366	299
ΔEN	1.9	0.9	0.7	0.4

From the above data it is observed that HF molecule has higher bond energy (567 kJmol⁻¹) due to greater electronegativity difference i.e. 1.9.

The smaller the size of the bonded atoms, the greater is the bond energy and stronger is the bond. The bond energy of H-H bond is 436 kJmol⁻¹ and that Cl-Cl is 242 kJmol⁻¹. It is due to the shorter bond length in H₂ molecule and greater bond length in Cl₂ molecule (larger size of Cl atom than H atom).

Multiple bonds also affect the bond energy, **greater the no. of bonds greater will be the bond energy.**

Table 3.1: Average Bond energies (kJmol⁻¹) of single bonds.

Bond	Bond Energy (kJmol ⁻¹)	Bond	Bond Energy (kJmol ⁻¹)	Bond	Bond Energy (kJmol ⁻¹)	Bond	Bond Energy (kJmol ⁻¹)	Bond	Bond Energy (kJmol ⁻¹)
C-H	413	Si-H	323	H-H	436	S-H	339	Cl-F	253
C-C	348	Si-Si	226	H-F	567	S-F	327	Cl-Cl	242
C-N	293	Si-C	301	H-Cl	431	S-Cl	253	Br-F	237
C-O	358	Si-O	368	H-Br	366	S-Br	218	Br-Cl	218
C-F	485	N-N	163	H-I	299	S-S	266	Br-Br	193
C-Cl	328	N-O	201	H-O	463	O-O	146	I-Cl	208
C-Br	476	N-F	272	H-F	155	O-F	190	I-Br	175
C-I	240	N-Cl	200	H-N	391	O-Cl	203	I-I	151
C-S	259	N-Br	243			O-I	234		

Table 3.2: Average Bond energies of multiple bonds (kJmol⁻¹)

Bond	Bond Energy (kJmol ⁻¹)	Bond	Bond Energy (kJmol ⁻¹)
C = C	614	N = N	418
C $\equiv$ C	839	N $\equiv$ N	941
C = N	891	O = O	495
C = O	799	S = O	523
C $\equiv$ O	1072	S = S	418

Polar bonds are stronger than non-polar bonds and greater amount of energy is required to break these bonds. Due to ionic character, the strength of bond increases. Increase in strength of H-Cl bond or ionic character in H-Cl bond can be observed from the experimentally



determined values of H-H, Cl-Cl and H-Cl bond and theoretically calculated bond energy value of H-Cl bond. It involves the following steps:

Step (i) Calculation of bond energy contribution of one H atom.

$$\begin{aligned}
 \text{Bond energy of 1 mole of H-H bonds} &= 436 \text{ kJ} \\
 \text{or Bond energy of } 6.02 \times 10^{23} \text{ H-H bonds} &= 436 \text{ kJ} \\
 \text{or Bond energy of one H-H bond} &= \frac{436}{6.02 \times 10^{23}} \text{ kJ} \\
 &= 72.42 \times 10^{-23} \text{ kJ} \\
 \text{Bond energy contribution of one H atom} &= \frac{72.42 \times 10^{-23}}{2} \\
 &= 36.21 \times 10^{-23} \text{ kJ}
 \end{aligned}$$

Step (ii) Calculation of bond energy contribution of one Cl atom.

$$\begin{aligned}
 \text{Bond energy of 1 mole of Cl-Cl bonds} &= 242 \text{ KJ} \\
 \text{or Bond energy of } 6.02 \times 10^{23} \text{ Cl-Cl bonds} &= \frac{242}{6.02 \times 10^{23}} \text{ kJ} \\
 \text{Bond energy of one Cl-Cl bond} &= 40.19 \times 10^{-23} \text{ kJ} \\
 \text{Bond energy contribution of one Cl atom} &= \frac{40.19 \times 10^{-23}}{2} \text{ kJ} \\
 &= 20.09 \times 10^{-23} \text{ kJ}
 \end{aligned}$$

Step (iii) Calculation of bond energy of 1 mole of H-Cl bonds.

This calculation is based on the assumption that H-Cl bond is non polar.

$$\begin{aligned}
 \text{Bond energy of one H-Cl bond} &= \text{Bond energy of H-atom} + \text{Bond energy of Cl atom.} \\
 &= (36.21 \times 10^{-23} + 20.09 \times 10^{-23}) \text{ kJ} \\
 &= 56.3 \times 10^{-23} \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{Bond energy of } 6.02 \times 10^{23} \text{ H-Cl bonds} &= 56.3 \times 10^{-23} \times 6.02 \times 10^{23} \\
 &= 338.93 \text{ kJ}
 \end{aligned}$$

$$\text{Bond energy of one mole of H-Cl bonds} = 338.93 \text{ kJ/mole}$$

The relation between bond energy and electronegativity can be seen from theoretically calculated and experimentally determined values of HCl bond.

Theoretically calculated bond energy of H-Cl bond = 338.93 kJ mol⁻¹.

Experimentally determined energy of H-Cl bond = 431 kJ mol⁻¹.

The experimentally determined bond energy is significantly greater than the calculated value, which means a more stable H-Cl bond. This stability is due to the ionic character present in the bond. The amount of additional bond energy depends on the electronegativity of the two bonded atoms. **Greater the difference of electro-negativity between the two bonded atoms, the greater is the ionic character and stronger is the bond.**

Table 3.3: Comparison of experimental and theoretical bond energies

Bond	Bond energies kJmol ⁻¹ .			
	X=F	X=Cl	X=Br	X=I
X-X	155	242	193	151
H-X(Calculated)	293	338	311	291
H-X (observed)	567	431	366	299
Difference	274	95	55	08

This data clearly indicate the part played by electronegativity in the strength of a bond. Electrons are not equally shared between hydrogen and halogen atoms in HX. Since halogen atom is more electronegative, the bonded electron pair is more attracted towards halogen



atom. This develops polarity in H-X molecules which produces an additional attractive binding force.

Bond Length

Bond length may be defined as the distance between the nuclei of atoms joined by covalent bond. This distance between the bonded atoms is not constant, because the bonded atoms are always vibrating with respect to each other. Therefore, average of minimum inter nuclear distance is considered as bond length or bond distance. Thus bond length may also be defined as the internuclear distance when the maximum possible overlap of concerned atomic orbitals occurs. It is measured by techniques such as X-ray diffraction, neutron diffraction and microwave spectroscopy.

Measuring units

It is measured in Å or picometer: $1 \text{ pm} = 10^{-12} \text{ m}$, $100 \text{ pm} = 1 \text{ Å} = 10^{-10} \text{ m}$.

It is observed that its measurements may vary in accuracy but still similar bonds have fairly constant lengths in different molecules, variation generally being less than 1%. In most of the compounds, the C-C single bond length is very close to 1.54 Å . For example in ethane molecule the C-C bond length is 1.54 Å and in ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$) the C-C bond length is 1.55 Å .

One half of the bond length between nuclei of two similar atoms join by single covalent bond is called the covalent radius of that atom. For example, the covalent radius of Carbon is 0.77 Å i.e. half of the C-C bond length which is 1.54 Å . The covalent-radii of other atoms are given in the following table:

Table 3.4: Covalent-radii of various atoms

Atom	Covalent-radius Å	Atom	Covalent-radius Å
H	0.28	F	0.72
C	0.77	Cl	0.99
N	0.75	Br	1.14
O	0.74	I	1.33

The covalent-radii can be used to calculate the bond length between two unlike atoms, which in some cases, is equal to the sum of the covalent radii of the two bonded atoms. For example, the C-Cl bond length in CH_3Cl is 1.76 Å , which is exactly the sum of the covalent radii of carbon (0.77 Å) and chlorine is (0.99 Å). However, in most cases, the length of a bond between two unlike atoms is markedly shorter than the sum of the two covalent radii. For example, the covalent radii of C and N add up to 1.52 Å where as the observed C-N bond length in methylamine (CH_3NH_2) is 1.47 Å . Similarly, the observed C-O bond length is ethanol ($\text{C}_2\text{H}_5\text{OH}$) is 1.42 Å , although the sum of the covalent radii of carbon and oxygen is 1.51 Å . In general, the shrinkage in bond length becomes more and more marked as the difference in electronegativity of the two bonded atoms increases.

Average single bond lengths of some of the important covalent bonds are given in the following table:



Table 3.5: Bond lengths of some Covalent Bonds

Covalent Bond	Bond Length Å	Covalent Bond	Bond Length Å
C-H	1.07	C-Br	1.93
C-C	1.54	C-I	2.14
C-O	1.42	C-Cl	1.76
C-N	1.47	O-H	0.96
C-F	1.38	N-H	1.01

Bond length is also affected by the nature of hybridization of the bonded atoms as shown in the following table:

Table 3.6: Effect of Hybridization on the Bond Length

Hybridization of Carbon	Bond Length (Å)		
	C-H	C-O	C-N
sp ³	1.11 (methane)	1.41 (ethanol)	1.47 (methylamine)
sp ²	1.10 (ethylene)	1.34 (formic acid)	1.36 (formamide)
sp	1.08 (acetylene)		

It can be noticed that the bonds are shortened by increasing "s" character. This is because the hybrid orbital with increased "s" character is held more tightly by the nucleus. A double bond between two atoms is shorter than a single bond between the same two atoms and a triple bond is shorter than the double bond as shown in the following table:

Table 3.7: Single, Double and Triple Bond Lengths.

Bonded atoms	Bond Length (Å)		
	Single bond	Double bond	Triple bond
C,C	1.54	1.38	1.19
C,N	1.47	1.28	1.16
C,O	1.42	1.20	---

This shrinkage of the multiple bonds is due to the presence of extra π electrons (two in the case of a double bond and four in the case of triple bond) between the two nuclei, which exert additional attraction on both the nuclei bringing them closer to each other.

Dipole Moment

(Determination of degree of polarity of molecules)

The degree of polarity of a molecule can be expressed in terms of dipole moment. **It is the product of the magnitude of the charge (positive or negative) and the distance between them.** If q is the charge at each end of dipole and r is the distance between the positive and negative centers, then dipole moment represented as μ is given by $\mu = q \times r$

Units: Its SI unit is Coulombs meter (C.m) but most common units used is Debye (D)

$$1 \text{ Debye (D)} = 3.336 \times 10^{-30} \text{ C.m}$$

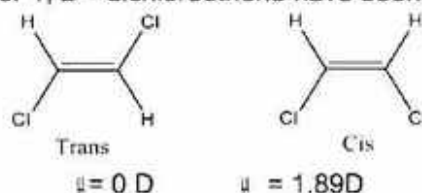
**Application of dipole moment****(i) Determination of polarity of molecule**

Molecules which have zero dipole moment are non-polar, Whereas molecules which have dipole moment are polar.

For example benzene has zero dipole moment, so it is non polar. But Chlorobenzene has dipole moment of 1.2D, so it is polar.

(ii) Prediction of isomers

The study of dipole moment also finds applications in stereochemistry. For example, dipole moments of isomer 1, 2 – dichloroethene have been calculated are given below:



Thus knowing the dipole moment of the given sample of 1, 2 – dichloroethene, one can predict whether it is Cis or trans isomer.

(iii) Calculation of %age ionic character in a bond.

The dipole moment helps to calculate the percentage ionic character in a bond.

Example

The observed dipole moment of HF is 1.90D. Find the percentage ionic character in HF bond. The distance between the charges is $0.917 \times 10^{-10} \text{ m}$.

(Unit positive charge = $1.6022 \times 10^{-19} \text{ C}$)

Solution:

Let us suppose that HF molecule is 100% ionic. It means that H has full positive charge and F has full negative charge. To calculate their dipole moments multiply the bond length with full charges of electron or proton i.e. 1.6022×10^{-19} . This dipole moment is called μ_{ionic} .

$$\begin{aligned}
 \text{So, } \mu_{\text{ionic}} &= q \times r \\
 &= (1.6022 \times 10^{-19} \text{ C}) (0.917 \times 10^{-10} \text{ m}) \\
 &= 1.469 \times 10^{-29} \text{ C.m}
 \end{aligned}$$

$$\text{Since } 1 \text{ D} = 3.336 \times 10^{-30} \text{ C.m}$$

$$\text{So, } \mu_{\text{ionic}} = \frac{1.469 \times 10^{-29} \text{ C.m}}{3.336 \times 10^{-30} \text{ C.m}} = 4.4 \text{ D}$$

The actual dipole moment as it is observed.

$$\mu_{\text{observed}} = 1.90 \text{ D}$$

$$\% \text{ ionic character} = \frac{1.90 \text{ D} \times 100}{4.4 \text{ D}} = 43.2\%$$

Hence HF bond is 43% ionic and 57% covalent. The bond is predominantly covalent.

3.4 EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS

The properties of substances are characterized by the type of bond present in them.

We shall consider the effects of the types of bond on physical and chemical properties of compounds.



Properties of Compounds:

Solubility

(a) Solubility of Ionic Compounds:

Most ionic compounds are soluble in water but insoluble in non-aqueous solvents.

Reason: When a crystal of ionic compound is placed in water, the polar water molecules detach the cation and anion from the crystal lattice by their electrostatic attraction. The ions are freed from the crystal lattice by hydration. This happens when the hydration energy is equal to or greater than the lattice energy. The energy released in hydration is used to overcome the lattice energy. Thus the ions are freed from their positions in the crystal.

Many ionic compounds do not dissolve in water because the attraction of water molecules cannot overcome the attraction between the ions. Their lattice energy dominates over their hydration energy. For the same reasons, the non-polar solvents benzene and hexane do not dissolve in ionic compounds.

(b) Solubility of Covalent Compounds:

Covalent compounds dissolve in non-polar organic solvents such as benzene, ether. Most covalent compounds are insoluble in water. However, some of them dissolve in water.

Reason: The attractive forces of solvent molecules in non-polar solvents are enough for overcoming the intermolecular forces of attraction in covalent compounds. Hence covalent compounds dissolve easily in non-polar organic solvents.

The solubility of covalent compounds in water depends on their ability to form hydrogen bonds with water molecules. Many organic compounds containing oxygen or nitrogen like carbohydrates, alcohols and amines are soluble in water due to hydrogen bonding.

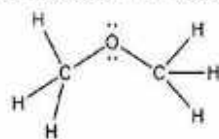
(c) Non-directional nature of ionic compounds:

Ionic bonds are non-directional and rigid in nature. They do not show the phenomenon of isomerism.

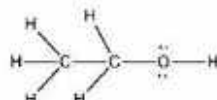
(d) Directional Nature of covalent compounds

Covalent bonds are non-rigid and directional. They show the phenomenon of isomerism.

Reason: Due to non-rigid and directional nature of the covalent bond, covalent compounds have different orientation of atoms in space. Hence many covalent compounds show the phenomenon of isomerism. For example C_2H_6O show structural isomerism.



Dimethyl Ether



Ethyl alcohol

3. Reaction Kinetics

(a) Speed of reaction of ionic compounds

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occurs rapidly. The reaction is so rapid because no bond is to be broken, only a new bond is formed. The ionic bonds have already been broken during the formation of solution.

For example, addition of silver nitrate solution to sodium chloride solution produces a



white precipitate of silver chloride instantaneously.

The oppositely charged ions combine at once to give the product. This is because no force is required to break the bonds of reacting compounds.

(b) *Speed of reaction of covalent compounds.*

Since there is no strong electrical force to speed up a chemical reaction, like in ionic reaction the covalent bonds are generally much slower to react as they involve both breaking and making of bonds. The molecules undergo a chemical change as a whole. It is because high energy is required to break the covalent bonds. Covalent compounds react in a variety of ways. The reactivity of covalent compounds depends upon the way a reaction proceeds and the kind of product-obtained at the end of a reaction.

4. Density:

The electrostatic force of attraction existing between the cations and anions in an ionic crystal brings these ions very close to one another. This decreases the volume of the crystal and consequently the ionic crystals have high density.

5. Types of Solids:

A solid is a structural unit of atoms, molecules or ions, which are held together strongly enough to give a rigid structure.

Four types of solids exist namely

(a) *Molecular solids:*

Consists of atoms or molecules held together by inter-molecular forces. Solid water (ice) and solid CO_2 (dry ice) are common examples.

(b) *Metallic Solids:*

Consists of atoms held together by metallic bonding, examples silver, copper and gold.

(c) *Ionic Solids:*

Consists of cations and anions held together by virtue of electrostatic attraction of the opposite charges. Examples are NaCl and CaCl_2 .

(d) *Covalent Network Solids:*

Consists of atoms held together in large network or chains by covalent bonds. Diamond and graphite are typical examples.

Difference between metallic Solids and Molecular Network Solids *Metallic Solids*

Metallic Solids

Metallic solids consist of infinite arrays of bonded atoms; each cation in a metal has a high co-ordination number sometimes four or six, but more often eight or twelve they are good conductors of electricity.

Covalent Network Solids

They consist of infinite arrays of bonded atoms; no individual molecules can be distinguished. Thus any given piece of network solid may be considered a giant, covalently bonded molecule. Network solids generally are poor conductor of heat and electricity. Strong covalent bonds among neighbouring atoms throughout the structure give these solids, strength and high melting temperature. Some of the hardest substances known are covalent network solids.

Diamond, the hardest allotrope of carbon, has the covalent network structure shown in the diagram. Diamond sublimes at 3500°C and above.



Graphite, a softer allotrope of carbon has three layered structure shown in the diagram.

One feature that distinguishes covalent network solids from metals is the lower co-ordination number of atoms in network structures. For example; Co-ordination number of C in diamond is four, silicon (Si) is four and that of oxygen in quartz is two.

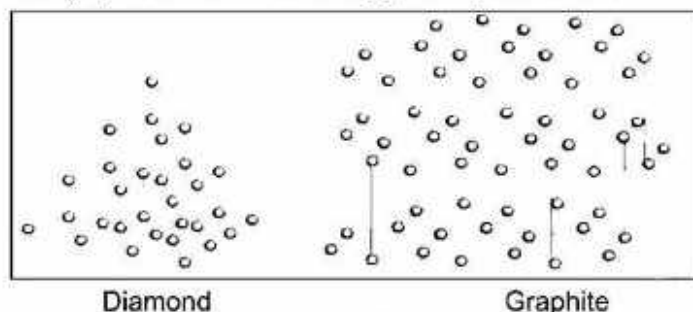
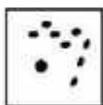


Figure 3.27: Allotropic forms of carbon

References for additional information

- John C. Kotz, Paul M. Treichel and Gabriela C. Weaver, Chemistry and Chemical reactivity.
- Asim and K. Das, Fundamental concepts of chemistry.
- David E. Goldberg, Fundamentals of Chemistry.
- Graham Hill and John Holman, Chemistry in context.



1. Choose the correct answer (MCQ).

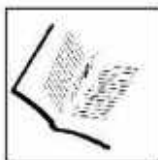
- (i) The bond energies of F_2 , Cl_2 , Br_2 , and I_2 are 37, 58, 46 and 36 k Cals, respectively. The strongest bond formed is in;
 - (a) F_2
 - (b) Cl_2
 - (c) I_2
 - (d) Br_2
- (ii) The percentage of ionic character of bond between two atoms is calculated from their;
 - (a) Dipole moment
 - (b) Electronegativities
 - (c) Electron affinities
 - (d) Ionization energies
- (iii) The geometry of PF_5 molecules is;
 - (a) Planar
 - (b) Square planar
 - (c) Trigonal bipyramidal
 - (d) Tetrahedral
- (iv) sp^3 hybridization is not important in describing the bonding in;
 - (a) NH_4^+
 - (b) CCl_4
 - (c) H_2O
 - (d) $AgCl$
- (v) Greater the dipole moment
 - (a) Greater is the ionic nature
 - (b) Lesser is the polarity
 - (c) Smaller is the ionic nature
 - (d) None
- (vi) A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is $1.0 \text{ \AA}$, what fraction of electric charge 'e' exist on each atom?
 - (a) 12% e
 - (b) 18% of e
 - (c) 25% e
 - (d) 30% of e



- (vii) H – O – H bond angle in H_2O is 104.5° and not 109.5° because of;
 (a) High electronegativity of oxygen (b) Bond pair – bond pair repulsion
 (c) Lone pair – lone pair repulsion (d) Lone pair – bond pair repulsion
- (viii) Which is not characteristic of π bond?
 (a) π bond is formed when a sigma bond already exist
 (b) π bond are formed from hybrid sp orbitals
 (c) π bond may be formed by the parallel overlapping of p-orbitals
 (d) π bond results from lateral overlap of atomic orbitals.
- (ix) In the formulation of N_2^+ from N_2 , the electron is removed from;
 (a) σ_{2p_x} orbital (b) $\sigma_{2p_x}^*$ orbital (c) π_{2p_y} orbital (d) $\pi_{2p_y}^*$ orbital
- (x) According to VESPR theory, the most probable shape of the molecule having 4 electron pairs around the central atom is;
 (a) Hexagonal (b) Tetrahedral (c) Octahedral (d) Linear
- 2 Read the given table below and answer the following questions.

Bond	Bond energies in kJmol^{-1}	
	X = Cl	X = I
X – X	242	151
H – X (Calculated)	336	291
H – X (Observed)	431	299
Difference	95	08

- (a) Give reason for the difference in calculated values and observed values.
 (b) Effect of high bond energy on bond length with reason.
 (c) Ionic character on the basis of bond energies, with reason.
3. Energies of orbitals can be explained by molecular orbital theory. It has been observed that in case of Nitrogen molecule σ_{2p_x} is higher in energy than π_{2p_y} and π_{2p_z}
 (a) Draw molecular orbital energy diagram for nitrogen molecule.
 (b) Give reason why the σ_{2p_x} energy is greater than π_{2p_y} and π_{2p_z} .
4. Carbon can make a bond with hydrogen to form ethyne. Bond energy of C–H is same although 2s and 2p orbitals are involved which have difference in energies. Explain the formation of ethyne molecule on the basis of hybridization with the help of diagram.
5. Molecular orbital theory can explain the magnetic character of O_2 , O_2^{2+} and O_2^{2-} species Evaluate it.
6. The melting points, boiling points, heat of vaporization and heats of sublimation of electrovalent (ionic) compounds are higher as compared to those of covalent-compounds. Argue.
7. The dipole moment of HCl is 1.03D and the distance between atoms is 127pm calculate the percentage of ionic character of the HCl bond. (Ans. 16.9%)
8. Differentiate between a sigma bond and a pi bond.
9. A double bond is stronger than a single bond and a triple bond is stronger than a double bond.



4

GASES



After completing this lesson, you will be able to:

This is 10 days lesson
(period including homework)

- List the postulates of Kinetic Molecular Theory.
- State the values of standard temperature and pressure (STP). Relate
- Define pressure and give its various units.
- Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin.
- State and explain the significance of Avogadro's Law.
- Derive Ideal Gas Equation using Boyle's, Charles' and Avogadro's law.
- Explain the significance and different units of ideal gas constant.
- Distinguish between real and ideal gases.
- Derive new form of Gas Equation with volume and pressure corrections for real gases.
- State and use Graham's Law of Diffusion.
- State and use Dalton's Law of Partial Pressures.
- Explain Lind's method for the liquefaction of gases.
- Define and explain plasma formation.
- Describe the motion of particles of a gas according to Kinetic Theory.
- Related temperature to the average kinetic energy of the particles in a substance
- Use Kinetic Theory to explain gas pressure.
- Describe the effect of change in pressure on the volume of gas.
- Describe the effect of change in temperature on the volume of gas.
- Define and describe the properties of Plasma
- Describe some of the implications of the Kinetic Molecular Theory, such as the velocity of molecules and Graham's Law.
- Explain why real gases deviate from the gas laws.

INTRODUCTION

Matter consists of three fundamental states, the gas, liquid and solid. Besides these three states, the fourth one is Plasma state (a partially ionised gas at very high temperature).

The word gas is derived from chaos. This is because the gaseous particles have chaotic (random) motion. The molecules travel in a straight line until they collide with each other or with the walls of the container. This type of motion of the molecules is called **Brownian Movement** (Robert Brown 1827).

A gas at a given temperature has neither a definite shape nor a definite volume. It will

take up the shape of any container into which it is placed.

All gases diffuse to fill the space available to them. The rates of diffusion are different for different gases. When diffusion takes place between a liquid and a gas, it is known as "intimate mixing".

The earth's atmosphere is a mixture of gases. Oxygen (21%) and Nitrogen (78%) are its two major components, both support life. In fact, the earth's atmosphere is an immense system of gases where many chemical reactions occur. For example, photo-synthesis, combustion etc. Natural gas, the major component of which is methane, is used to heat homes in winter, to cook food and to drive vehicles etc.

4.1 KINETIC MOLECULAR THEORY OF GASES

The behaviour and properties of gases can be theoretically explained using the kinetic molecular theory. This theory is a model that explains the behaviour of gases using generalization about random moving molecules within a gas.

The kinetic molecular theory was first postulated by Daniel Bernoulli, a Swiss mathematician. The Kinetic theory of gases was elaborated and extended by a number of well-known physicist such as James Maxwell (1859) and Boltzmann in (1870). In 1857, Clausius derived the kinetic equation and deduced all the gas laws from it.

Physical theories are often given in terms of postulates, the basic statements from which all conclusions or prediction of theory is deduced.

The kinetic molecular theory of gases is based upon the following postulates:

1. Gases are considered to be composed of minute discrete particles called molecules.
2. The molecules move randomly in straight lines until they collide with one another or with the walls of container.
3. The collisions among the molecules are perfectly elastic i.e. the total kinetic energy remains constant.
4. The molecules of a gas are thought to be of the same mass and size but are different from gas to gas.
5. The pressure is produced due to the collisions of the molecules.
6. The average kinetic energy of a molecule is directly proportional to the absolute temperature. It means that the higher the temperature, greater will be the molecular kinetic energy.
7. At relatively low pressure, the average distances between molecules are large as compared with molecular diameters.
8. There are no attractive or repulsive forces between the molecules.
9. The volume occupied by the molecules is negligible as compared to the total volume of the container.

R.J. Clausius deduced an equation for the pressure of an ideal gas from the postulates of kinetic theory. This equation is called **kinetic equation**.

Mathematically, $PV = \frac{1}{3} mNc^2$

Where P = Pressure
 V = Volume
 m = mass of one molecule of the gas
 N = number of particles of the gas
 c^2 = mean square velocity of gas molecules

Since the molecules of a gas under the given conditions do not have the same velocity, so mean square velocity is considered. If n_1 molecules have velocity c_1 , n_2 molecules have velocity c_2 etc, then

$$c^2 = \frac{n_1 c_1^2 + n_2 c_2^2 + \dots}{n_1 + n_2 + \dots}$$

Where c^2 is the average of squares of all the possible velocities. The square root of c^2 is called root mean square velocity (C_{rms}).

According to the kinetic molecular theory, the gaseous molecules are always in a state of haphazard motion. As a result due to their motion, they will have certain kinetic energy. The increase or decrease of temperature will increase or decrease their motion. In gases, the molecular motion is of three types:

- i. Translational Motion.
- ii. Rotational Motion.
- iii. Vibrational Motion.

A mono atomic molecule (e.g. He) will show only translational motion while a diatomic (H_2) and polyatomic molecules (CO_2 , NH_3 etc.) will undergo, in addition to translational motion, the rotational and vibrational motions too.

i. Translational Motion:

The motion imparted to the gaseous molecules due to their motion in all possible directions is called translational motion and the energy as kinetic translation energy. In this case the entire molecules move from place to place.

ii. Rotational Motion:

The motion imparted to the gaseous molecules as a result of net angular momentum about their centre of gravity is called rotational motion and the energy as kinetic rotational energy. In this case the molecule spins like a propeller.

iii. Vibrational Motion:

The motion imparted to the gaseous molecules due to the oscillations is called vibrational motion and the energy as kinetic vibrational energy. In this case the molecules vibrate back and forth about the same fixed location.

In such an oscillating system, there is a continuous interchange between vibrational kinetic energies and potential energies. As a result both K.E and P.E is possessed by the gaseous molecules. Thus, $Total E(Vib.) = K.E (Vib.) + P.E (Vib.)$

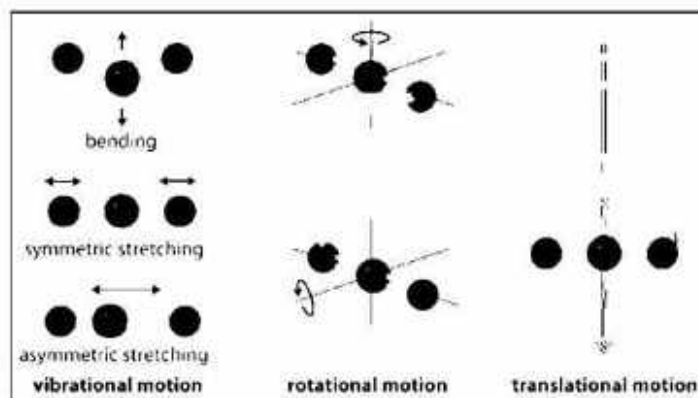


Figure 4.4: Different motions of molecules

The vibrational motions in polyatomic molecules (like CO_2 , NH_3 etc.) are quite complicated.

4.2 ABSOLUTE TEMPERATURE SCALE ON THE BASIS OF CHARLE'S LAW

The Charle's Law states that the volume of a given mass of a gas increases or decreases by $1/273$ times of its original volume at 0°C and reduces to zero at -273.15°C . Actually at this temperature a gas does not remain in gaseous state but changes into the liquid or a solid.

Lord Kelvin (1824-1907) succeeded in measuring temperature of the gas with the help of a new scale called the Absolute Kelvin temperature scale or the Kelvin temperature scale. According to this scale, -273.15°C is the starting point of the scale. On comparing with the Celsius scale, (which starts with 0°C), the two scales are related as

$$K = ^\circ\text{C} + 273$$

Example 4.1

Convert the following Celsius temperatures to Kelvin temperatures:

- (a) -132°C (b) 96°C (c) 0°C (d) -12°C (e) 148°C

Solution

Using the formula: $K = ^\circ\text{C} + 273$

- (a) $K = -132 + 273 = 141 \text{ K}$ (b) $K = 96^\circ\text{C} + 273 = 369 \text{ K}$
 (c) $K = 0^\circ\text{C} + 273 = 273 \text{ K}$ (d) $K = -12^\circ\text{C} + 273 = 261 \text{ K}$
 (e) $K = 148^\circ\text{C} + 273 = 421 \text{ K}$

Example 4.2

Convert the following Kelvin temperatures to Celsius degree centigrade temperatures.

- (a) 340 K (b) 200 K (c) 10 K (d) 405 K

Solution:

Using the formula: $t^\circ\text{C} = K - 273$

- (a) $t^\circ\text{C} = 340 - 273 = 67^\circ\text{C}$ (b) $t^\circ\text{C} = 200 - 273 = -73^\circ\text{C}$
 (c) $t^\circ\text{C} = 10 - 273 = -263^\circ\text{C}$ (d) $t^\circ\text{C} = 405 - 273 = 132^\circ\text{C}$

The temperature of a gas depends upon kinetic energy of the molecules. The increase of temperature increases the average kinetic energy of the molecules and vice versa.

Derivation of relationship between Kinetic Energy and Temperature

The average kinetic energy of the gaseous molecules is re-distributed with rise or fall of temperature. It can be explained with the help of kinetic equation of gases.

According to kinetic equation of gases,

$$PV = \frac{1}{3} m N \overline{c^2} \quad \dots\dots\dots (1)$$

$$\text{and } K.E = \frac{1}{2} m \overline{c^2} \quad \dots\dots\dots (2)$$

$$\begin{aligned} \text{Again we consider } PV &= \frac{1}{3} m N \overline{c^2} \\ &= \frac{2}{3} N \left(\frac{1}{2} m \overline{c^2} \right) \\ &= \frac{2}{3} N (K.E) \quad \dots\dots\dots (3) \end{aligned}$$

Now consider one mole of gas. It will possess Avogadro's number (N_A) of molecules,

Then $N = N_A$

$$\text{Therefore } PV = \frac{2}{3} N_A (K.E) \quad \dots\dots\dots (4)$$

According to the General Gas Equation

$$PV = nRT \quad \dots\dots\dots (5)$$

For one mole of a gas, $n = 1$ then $PV = RT$

Comparing equations (4) & (5) we get,

$$\frac{2}{3} N_A (K.E) = RT \quad \dots\dots\dots (6)$$

$$2N_A (K.E) = 3RT$$

$$K.E = \frac{3RT}{2N_A}$$

$$K.E = kT, \text{ where } \frac{3R}{2N_A} = k, \text{ a constant quantity.}$$

$$\text{or } K.E \propto T$$

Conclusion

The Kelvin Temperature of a gas is actually the measure of average translational K.E of its molecules.

In gases and liquids, the temperature explains the average translational energy of the molecules. In solids where molecules cannot move freely, temperature becomes a measure of vibrational K.E.

According to the Kinetic molecular theory, gas molecules are in constant random motion. They move in straight line until they collide with another molecule or the walls of the container. The pressure of a gas in a container is due to the force exerted by its molecules on the walls of the container. The average kinetic energy of gas molecules is directly proportional to the Kelvin

temperature. So the average kinetic energy of a collision when a gas molecule collides with the walls of a container will not change at constant temperature.

Gaseous pressure and its various units

When a balloon is inflated, its walls expand. The balloon walls tend to collapse due to the squeezing of air trapped inside. However this must be counterbalanced by a force exerted by the trapped gas. This force is called Pressure.

So a **force being exerted over a unit area is called Pressure.**

So, $P = \frac{F}{A}$ where P is measured in Pascal, Force in Newton and the area in m^2 .

A Pascal (Pa) is defined as the force of one Newton (N) spread over an area of $1m^2$.

Units of Pressure:

SI Units:

SI unit for pressure is Pascal (Pa), in S.I. system, unit of force is Newton (N) and the unit of area is metre square (m^2). Thus Pascal is one Nm^{-2} .

1 atm	= 101325 Pa = 101325 Nm^{-2}
1 atm	= 14.7 Psi (Pounds per square inch)
1 atm	= 101.325 kPa
1 atm	= 760 torr = 760 mm of Hg
1 J	= 1 Nm = 10^7 ergs = kgm^2s^{-2}
1 Cal	= 4.18 J
1 atm	= 1.01325 bar

Interconversion of Pressure in Pascals, Kilo Pascals and atmosphere

Example 4.3

Convert 10 Pascals into (i) Kilo Pascals (ii) atmosphere

Solution:

(i) One Kilo Pascal = 1000 Pascals
or 1000 Pascals = one Kilo Pascal
 $10 \text{ Pa} = \frac{1}{1000} \times 10 = 0.01 \text{ Kilo Pascal}$

(ii) One atmosphere = 101325 Pa
or 101325 Pa = one atm
 $10 \text{ Pa} = \frac{1}{101325} \times 10 = 0.000098 \text{ atm}$



Self Check Exercise 4.1

Example: Convert 35 Psi into (i) Pascal (ii) Kilo Pascal (iii) Atmosphere

In the middle of the 17th century, Robert Boyle (1627-1691) and his assistant Robert Hooke (1635-1702) made many investigations about the relationship between Pressure and Volume of a gas. In 1662, Robert Boyle reported that with increase in pressure on a gas, its volume

decreases. This was stated as Boyle's Law. It states that the pressure of a fixed amount of a gas varies inversely with its volume, the temperature is maintained constant.

Mathematically, $P \propto \frac{1}{V}$ or $P = k \times \frac{1}{V}$ where k is proportionality constant. The value of k is different for different amounts of the same gas.

Again $P = k \times \frac{1}{V}$ or $PV = k$, thus the product of volume and Pressure remains constant provided the temperature is kept constant.

$$P_1 V_1 = k \text{ (For gas at pressure } P_1 \text{)}$$

$$P_2 V_2 = k \text{ (For gas at pressure } P_2 \text{)}$$

Therefore $V_1 P_1 = V_2 P_2$ where V_1 and P_1 are initial volume and Pressure while P_2 and V_2 are their final Pressure and volume.

When the Pressure of a gas is plotted against volume at different temperatures, we get a family of curves as shown in the figure 4.7. Each curve is a hyperbola with different values of k . Each curve is known as Isotherm (constant temperature plot). As the temperature is increased, the Isotherm goes away from both the axis. This is because at higher temperature, the volume of the gas is increased.

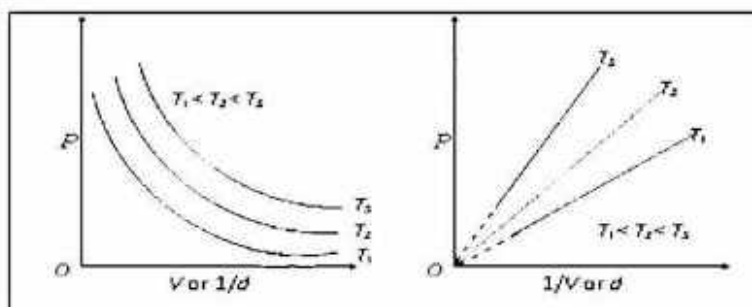


Figure 4.7: Graphical representation of different forms of Boyle's Law

Example 4.4

An ideal gas occupies a volume of 0.300 dm^3 at a pressure of $1.80 \times 10^5 \text{ Pa}$. What is the volume of the gas maintained at the same temperature if the pressure is reduced to $1.15 \times 10^5 \text{ Pa}$.

Solution

$$V_1 = 0.300 \text{ dm}^3 \quad V_2 = ?$$

$$P_1 = 1.80 \times 10^5 \text{ Pa} \quad P_2 = 1.15 \times 10^5 \text{ Pa}$$

According to the Boyle's Law

$$V_1 P_1 = V_2 P_2$$

$$\text{or } V_2 = \frac{V_1 P_1}{P_2}$$

$$= \frac{0.300 \text{ dm}^3 \times 1.80 \times 10^5 \text{ Pa}}{1.15 \times 10^5 \text{ Pa}}$$

$$= \frac{0.300 \times 1.80}{1.15} \text{ dm}^3 = 0.469 \text{ dm}^3$$

Example 4.5

At sea level, where the pressure was 755 torr, the gas in a balloon occupied 2m^3 . What volume will the balloon expand when it has risen to an altitude where the pressure is

- (a) 100 torr (b) 10 torr temperature remains constant

Solution

(a) $P_1 = 755\text{ torr}$ $P_2 = 100\text{ torr}$

$V_1 = 2\text{m}^3$ $V_2 = ?$

According to the Boyle's Law

$$V_1 P_1 = V_2 P_2$$

$$2\text{m}^3 \times 755\text{ torr} = V_2 \times 100\text{ torr}$$

or $V_2 = \frac{2\text{m}^3 \times 755\text{ torr}}{100\text{ torr}}$

$$V_2 = \frac{2 \times 755}{100} \text{ m}^3 = 15.10\text{m}^3$$

(b) $V_1 = 2\text{m}^3$ $V_2 = ?$

$P_1 = 755\text{ torr}$ $P_2 = 10\text{ torr}$

According to the Boyle's law

$$V_1 P_1 = V_2 P_2$$

$$2\text{m}^3 \times 755\text{ torr} = V_2 \times 10\text{ torr}$$

or $V_2 = \frac{2\text{m}^3 \times 755\text{ torr}}{10\text{ torr}}$
 $= \frac{2 \times 755}{10} \text{ m}^3 = 151\text{m}^3$



Self Check Exercise 4.2

375cm^3 of a given gas has a pressure of 770mm of Hg. What will be the volume if the pressure is reduced to 750mm of Hg? (Ans: 385 cm^3)

The thermal expansion of gases was studied by Jacques Charles (1746-1823). He derived the relationship between volume of a gas and temperature in 1787. This relationship is known as Charles's law. **It states that at constant pressure, the volume of a given mass of a gas varies linearly with the absolute temperature of the gas.** Charles's law can also be stated as "at constant pressure the volume of given mass of gas increases or decreases by $\frac{1}{273}$ times of its original volume at 0°C for every 1°C rise or fall in temperature respectively."

From his preliminary investigations, Charles observed that the gases such as H_2 , CO_2 , O_2 etc. expanded equally on heating from $0^\circ C$ to $80^\circ C$ at constant pressure.

Derivation of critical form of Law

Suppose the volume of a gas at $0^\circ C = V_0$

$$\text{Volume at } 1^\circ C = V_0 + V_0 \frac{1}{273}$$

$$\text{Volume at } 2^\circ C = V_0 + V_0 \frac{2}{273}$$

$$\text{Volume at } t^\circ C = V_0 + V_0 \frac{t}{273}$$

$$V_t = V_0 \left[1 + \frac{t}{273} \right]$$

$$= V_0 \left[\frac{273 + t}{273} \right]$$

Where $t^\circ C + 273 = T$ (Absolute temperature)

$$= V_0 \left[\frac{T}{273} \right]$$

$$V_t = \frac{V_0}{273} T$$

Thus the Law states that the volume of a definite quantity of a gas at constant pressure is directly proportional to the absolute temperature.

Again $V \propto T$ or $V = kT$, where T is the temperature on absolute scale. Thus the temperature on degree centigrade or Celsius scale can be converted to the absolute scale or Kelvin scale (after the name lord Kelvin 1824-1907) by adding 273.15.

Thus $K = t^\circ C + 273.15$

Now $V = kT$ or $\frac{V}{T} = k$

Thus the Law may also be defined as, "the ratio between volume and temperature is always a constant quantity."

$$\text{So } \frac{V_1}{T_1} = k \quad \text{and} \quad \frac{V_2}{T_2} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where V_1 and T_1 are initial volume and absolute temperature. V_2 and T_2 are final volume and absolute temperature.

The equation for Charles's Law gives a straight line proved by plotting a graph between volume and temperature. Different straight lines are obtained with different pressures, which are a constant quantity. Each constant pressure line is called an "Isobar".

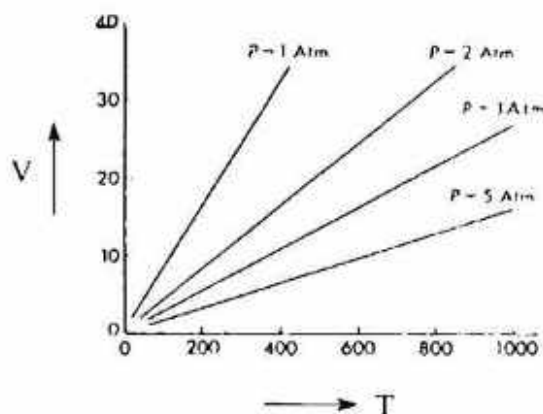


Figure 4.9: Graphical verification of Charles law

According to critical definition of Charles's Law, at constant pressure, the volume of given mass of a gas increases or decreases by $\frac{1}{273}$ of its original volume at 0°C by 1°C rise or fall of temperature, respectively.

Let the volume of an ideal gas at 0°C is $V_0 \text{ cm}^3$

$$\text{Volume at } -1^\circ\text{C} = V_0 - \frac{1}{273} V_0$$

$$\text{Volume at } -273^\circ\text{C} = V_0 - \frac{273}{273} V_0 = 0$$

Thus exactly at -273°C , the volume of a given mass of a gas reduces to zero. A graph between volume and temperature gives a straight line and cuts the temperature axis at -273.15°C .

Thus the **hypothetical temperature at which the given volume of a gas reduces to zero is called Absolute zero**. For this reason a new temperature scale has been developed. This new scale is called Absolute or Kelvin scale. It starts from -273.15°C which is marked as zero Kelvin.

$$-273.15^\circ\text{C} = \text{Zero Kelvin}$$

This is applicable for all other gases as well and is the lowest possible temperature in the gaseous state but actually it does not happen because all the gases liquify or solidify before they reach this temperature (-273.15°C). This temperature is considered as the lowest possible temperature.

Example 4.6

If 50 cm^3 of a gas in a syringe at 15°C is heated to 50°C and the piston of syringe is allowed to move outwards against constant atmospheric pressure, calculate the new volume of the hot gas.

Solution

$$V_1 = 50 \text{ cm}^3 \quad V_2 = ?$$

$$T_1 = 15^\circ\text{C} + 273 = 288\text{K} \quad T_2 = 50^\circ\text{C} + 273 = 323\text{K}$$

According to Charles's Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{50 \text{ cm}^3}{288\text{K}} = \frac{V_2}{323} \quad \text{or} \quad V_2 = \frac{50 \times 323}{288} \times \frac{\text{cm}^3 \times \text{K}}{\text{K}}$$

$$= 56 \text{ cm}^3$$

Therefore the new volume of the hot gas = 56 cm^3 .

Example 4.7

At 17°C , a sample of H_2 gas occupies 125 cm^3 . What would be the volume at 100°C ? (Pressure remains constant)

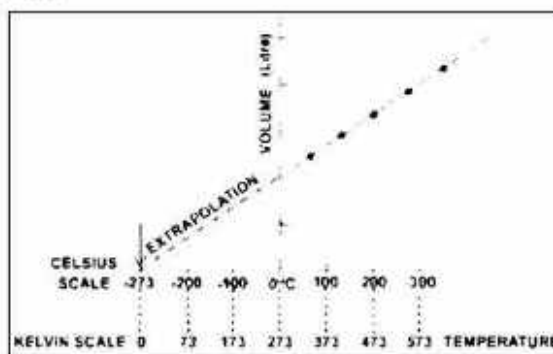


Figure 4.11: Effect of decrease of temp on a definite volume of a gas at constant pressure

Solution

$$V_1 = 125 \text{ cm}^3$$

$$T_1 = 17^\circ\text{C} + 273$$

$$= 290 \text{ K}$$

$$V_2 = ?$$

$$T_2 = 100^\circ\text{C} + 273$$

$$= 373 \text{ K}$$

According to Charles's Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{125 \text{ cm}^3}{290 \text{ K}} = \frac{V_2}{373 \text{ K}} \quad \text{or} \quad V_2 = \frac{125 \times 373}{290} \frac{\text{cm}^3 \times \text{K}}{\text{K}}$$

$$= 160.78 \text{ cm}^3$$

Thus the new volume will be 160.78 cm^3

**Self Check Exercise 4.3**

A Volume-Temperature experiment which was performed on a sample of H_2 gas produced the Charles's Law relationship $V = 0.167T$ (V is in dm^3). At what temperature in degree Celsius would this sample of gas occupy 50 dm^3 , if the pressure remains constant? (Ans: 26.40°C)

4.3 AVOGADRO'S LAW

An Italian Physicist Amedeo Avogadro (1776-1856) in 1811 proposed that a given volume of any gas at fixed temperature and pressure must contain the same number of independent units (particles). These particles may be atoms, molecules or both.

This means that if we take equal volumes of two gases at a fixed temperature and pressure, the number of molecules of both gases will always be the same. It means volume is directly proportional to the number of molecules, where v is volume of the gas and n are number of molecules, the independent entities.

Avogadro's Law states that equal volumes of all gases at the same temperature and pressure must contain equal number of molecules.

Mathematically $V \propto n$ or $V = K \times n$

The exact number of particles (atoms, molecules) has been calculated in one mole of a substance with the help of spectrometer and may be called as Avogadro's number, after the name of Avogadro. It is numerically equal to 6.022×10^{23} particles per mole. It was confirmed by Joseph Loschmidt (1821-1895). In the case of mono-atomic gases, it should be 6.022×10^{23} atoms mole^{-1} and 6.022×10^{23} molecules mole^{-1} in the case of di- and poly-atomic molecules.

e.g. 1 mole of Hydrogen atom is equal to 1.008 g.

It contains 6.022×10^{23} atoms of hydrogen. However one mole of H_2 gas having molecular mass as 2.016g will contain 6.022×10^{23} molecules.

Now it has been calculated that if we have one dm^3 of H_2 , its mass will be 0.09g at S.T.P.

$$\therefore 0.09\text{gH}_2 \text{ at S.T.P} = 1\text{dm}^3$$

$$2.016\text{gH}_2 \text{ (one mole) at S.T.P} = \frac{1}{0.09} \times 2.016\text{dm}^3 = 22.4\text{dm}^3$$

Thus 1gram molecule or one mole of H_2 will have 22.4dm^3 at S.T.P. This volume of 22.4dm^3 at S.T.P is called Molar volume.

Generally one mole of any gas at S.T.P. occupies a volume of 22.4dm^3 . But one mole of the same gas will contain 6.022×10^{23} molecules. Other examples are as following:

$$1 \text{ mole of } \text{N}_2 \text{ (28 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

$$1 \text{ mole of } \text{Cl}_2 \text{ (71 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

$$1 \text{ mole of } \text{O}_2 \text{ (32 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

$$1 \text{ mole of } \text{CO}_2 \text{ (44 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

The standard temperature is 0°C and pressure is one atmosphere.

Example 4.8

Calculate the (i) number of molecules and atoms (ii) Number of mole (iii) Volume in dm^3 of 10g of ammonia at S.T.P.

Solution:

(i) Number of molecules and atoms

According to Avogadro's Law, one mole of any gas at S.T.P. contains 6.022×10^{23} molecules in case of di-atomic and poly-atomic molecules. For example, in the case of ammonia one mole of it contains 6.022×10^{23} molecules.

$$\text{Now mass of } \text{NH}_3 = 10\text{g}$$

$$\text{Number of moles of } \text{NH}_3 = \frac{\text{mass}}{\text{molecular mass}} = \frac{10}{17} = 0.588 \text{ moles}$$

$$\text{One mole of } \text{NH}_3 \text{ at S.T.P.} = 6.022 \times 10^{23} \text{ molecules.}$$

$$\begin{aligned} 0.588 \text{ moles of } \text{NH}_3 \text{ at S.T.P.} &= 0.588 \times 6.022 \times 10^{23} \text{ molecules} \\ &= 3.54 \times 10^{23} \text{ molecules} \end{aligned}$$

$$\text{Now number of atoms} = \text{no of molecules} \times \text{atomicity (Number of atoms in one molecule of } \text{NH}_3)$$

$$= 3.54 \times 10^{23} \times 4$$

$$= 14.16 \times 10^{23} \text{ atoms}$$

(ii) Volume in dm^3

We know that

$$22.414\text{dm}^3 \text{ of any gas at S.T.P} = 1 \text{ mole}$$

$$22.414\text{dm}^3 \text{ of } \text{NH}_3 \text{ at S.T.P} = 17\text{g}$$

$$\text{or } 17\text{g } \text{NH}_3 = 22.4\text{dm}^3$$

$$10\text{g } \text{NH}_3 = \frac{22.414}{17} \times 10 = 13.184 \text{ dm}^3$$

**Self Check Exercise 4.4**

Calculate the number of molecules in (i) 1dm^3 of oxygen (ii) 2dm^3 of Hydrogen (iii) 2.5dm^3 of nitrogen All gases are at S.T.P.

(Ans: (i) 2.7×10^{22} (ii) 5.4×10^{22} (iii) 6.75×10^{22})

4.4 IDEAL GAS EQUATION OR EQUATION OF STATE FOR AN IDEAL GAS

An equation that shows the effects of simultaneous changes in pressure and temperature on the volume of given amount of a gas is called ideal gas equation or equation of state for an ideal gas.

The ideal Gas Equation is a combination of three Laws:

1. Boyle's Law 2. Charles's Law 3. Avogadro's Law

Now according to Boyle's Law

$$V \propto \frac{1}{P} \quad (\text{at constant } T \text{ and } n) \quad (1)$$

According to Charles's Law

$$V \propto T \quad (\text{at constant } P \text{ and } n) \quad (2)$$

According to Avogadro's Law

$$V \propto n \quad (\text{at constant } P \text{ and } T) \quad (3)$$

Where n is the number of moles of the gas.

Combining equations (1), (2) and (3), we get

$$V \propto \frac{1}{P} nT \quad V \propto \frac{nT}{P} \quad V = R \frac{nT}{P}$$

or

$$PV = nRT$$

Where R is a constant called general gas constant. This equation is called general gas equation or ideal gas equation.

$$\text{If } n = 1 \quad \text{Then } PV = RT \quad \text{or} \quad \frac{PV}{T} = R$$

$$\text{So} \quad \frac{P_1 V_1}{T_1} = R \quad (\text{For first condition of gas})$$

$$\text{and} \quad \frac{P_2 V_2}{T_2} = R \quad (\text{For second condition of gas})$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$



4.1.1 Standard temperature and pressure

Ideal gas equation enables us to calculate the effect of a change in temperature and pressure on the volume of a gas. One cannot compare volumes unless they are stated at the same temperature and pressure. Gas volumes are usually compared at 0°C (273K) and 1 atm. These conditions are referred to as standard temperature and pressure (STP).

Example 4.9

A certain mass of a gas occupies 1000 cm³ at 57°C and 726 mm of Hg. What will be the volume at S.T.P?

Solution

$$\begin{array}{ll} V_1 = 1000 \text{ cm}^3 & V_2 = ? \\ P_1 = 726 \text{ mm of Hg} & P_2 = 760 \text{ mm of Hg} \\ T_1 = 57^\circ\text{C} + 273 & T_2 = 273\text{K} \\ = 330\text{K} & \end{array}$$

Now apply the general gas equation

$$\begin{aligned} \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \frac{726 \text{ mm of Hg} \times 1000 \text{ cm}^3}{330\text{K}} &= \frac{760 \text{ mm of Hg} \times V_2}{273\text{K}} \\ V_2 &= \frac{726 \text{ mm of Hg} \times 1000 \text{ cm}^3}{330\text{K}} \times \frac{273\text{K}}{760 \text{ mm of Hg}} \\ V_2 &= \frac{726 \times 1000 \times 273}{330 \times 760} \frac{\text{mm of Hg} \times \text{cm}^3 \times \text{K}}{\text{K} \times \text{mm of Hg}} \\ V_2 &= 790.3 \text{ cm}^3 \\ \text{So the volume of the gas at S.T.P} &= 790.3 \text{ cm}^3 \end{aligned}$$



Self Check Exercise 4.5

- Q.1** A given mass of a gas occupies 850 cm³ at 320K and 0.92 × 10⁵ Nm⁻² pressure. Calculate the new volume of the gas at S.T.P. (Ans: 658.410 cm³)
- Q.2** A container contains 2.5 m³ of Helium gas at 15°C and 98 Nm⁻² pressures. What volume would this gas occupy at S.T.P? (Ans: 2.3 × 10⁻³ m³)

With the help of the Ideal Gas equation, we can determine:

- (a) Molecular mass of the gas. (b) Density of the gas.

(i) **Molecular Mass of the Gas:**

According to the general gas equation $PV = nRT$ (1)

But n (no of moles) = $\frac{W}{M}$ Where W = mass of the gas M = molecular mass of the gas

Putting the value of n in equation-1

$$PV = \frac{W}{M} RT$$

$$MPV = WRT$$

$$\text{or } M = \frac{WRT}{PV}$$

So molecular mass (M) can be calculated if P , V , W and T are known.

(ii) **Density of the gas (g dm^{-3}):**

According to the General Gas Equation, $PV = nRT$ (1)

but $n = \frac{W}{M}$, Therefore $PV = \frac{W}{M} RT$ or $MP = \frac{W}{V} RT$

as $\frac{W}{V} = d$ (density),

$$\text{so } MP = d RT$$

$$\text{or } d = \frac{MP}{RT} \quad \text{..... (2)}$$

So knowing the values of P , T and M , the density can be calculated.

Calculation of R value

The value of R can be calculated in different ways as shown below:

- (i) If one mole of a gas is taken at S.T.P (273 K, 1 atm), then the volume occupied by it is 22.4dm^3 . Now according to the general gas equation,

$$PV = nRT$$

Where $V = 22.4\text{dm}^3$ $P = 1\text{ atm}$ $n = 1\text{ mole}$ $T = 273\text{ K}$ Then $R = ?$

From the equation

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{22.4\text{ dm}^3 \times 1\text{ atm}}{1\text{ mole} \times 273\text{ K}}$$

$$R = \frac{22.4 \times 1}{1 \times 273} \text{ dm}^3 \times \text{atm mole}^{-1} \text{ K}^{-1}$$

$$R = 0.0821\text{ dm}^3\text{ atm mole}^{-1} \text{ K}^{-1}$$

- (ii) If pressure is measured in mm of Hg or torr and V in cm^3 then

$$R = 0.0821\text{ dm}^3 \times \text{atm mole}^{-1} \text{ K}^{-1}$$

$$= 0.0821\text{ dm}^3 \times 760\text{ mm of Hg mole}^{-1} \text{ K}^{-1}$$

$$= 62.4\text{ dm}^3\text{ mmHg mole}^{-1} \text{ K}^{-1}$$

$$= 62.4\text{ dm}^3\text{ torr mole}^{-1} \text{ K}^{-1} \text{ (one mm of Hg = one torr)}$$

$$= 62.4 \times 1000\text{ cm}^3 \text{ torr mole}^{-1} \text{ K}^{-1}$$

$$= 62400\text{ cm}^3\text{ torr mole}^{-1} \text{ K}^{-1}$$



(iii) In SI Units, pressure is expressed in Nm^{-2} and volume in m^3 , then

$$V = 0.0224 \text{ m}^3 \quad (1 \text{ dm}^3 = 10^{-3} \text{ m}^3)$$

$$P = 101325 \text{ Nm}^{-2}$$

$$n = 1 \text{ mole}$$

$$T = 273 \text{ K}$$

$$R = ?$$

$$R = \frac{VP}{nT}$$

$$= \frac{0.0224 \text{ m}^3 \times 101325 \text{ Nm}^{-2}}{1 \text{ mole} \times 273 \text{ K}}$$

$$= \frac{0.0224 \times 101325}{1 \times 273} \text{ m}^3 \text{ Nm}^{-2} \text{ mole}^{-1} \text{ K}^{-1}$$

$$R = 8.3143 \text{ Nm mole}^{-1} \text{ K}^{-1}$$

Now we know that $1 \text{ Nm} = 1 \text{ J}$

$$\text{So, } R = 8.3143 \text{ J mole}^{-1} \text{ K}^{-1}$$

Example 4.10

Calculate the average molar mass of air at sea level and 0°C if the density of air is 1.29 kg m^{-3} .

Solution:

At sea level the pressure may be taken equal to 1 atm or 101325 Pa. We know that

$$d = \frac{MP}{RT} \quad \text{or} \quad M (\text{average molar mass}) = \frac{dRT}{P} \quad (1)$$

$$\text{Where } d = 1.29 \text{ kg m}^{-3}$$

$$R = 8.3143 \text{ Nm mole}^{-1} \text{ K}^{-1}$$

$$T = 273 \text{ K}$$

$$P = 101325 \text{ Nm}^{-2}$$

Now putting the values of these in equation (1)

$$M = \frac{1.29 \text{ kg m}^{-3} \times 8.3143 \text{ Nm mole}^{-1} \text{ K}^{-1} \times 273 \text{ K}}{101325 \text{ Nm}^{-2}}$$

$$= \frac{0.0289 \text{ kg m}^{-3} \times \text{Nm mole}^{-1} \text{ K}^{-1} \text{ K}}{\text{N. m}^{-2}}$$

$$M = 0.0289 \text{ kg mole}^{-1}$$

Example 4.11

A certain gas occupies a volume of 6 dm^3 under a pressure of 720 mm of Hg at 25°C . What volume will this gas occupy under standard conditions of Temperature and Pressure (S.T.P)?

Solution

$$\begin{aligned}
 V_1 &= 6 \text{ dm}^3 & V_2 &= ? \\
 P_1 &= 720 \text{ mm} & P_2 &= 760 \text{ mm} \\
 T_1 &= 25^\circ\text{C} + 273 & T_2 &= 273 \text{ K} \\
 &= 298 \text{ K}
 \end{aligned}$$

According to the General Gas Equation

$$\begin{aligned}
 \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} & \text{or} & & V_2 &= \frac{P_1 V_1 T_2}{T_1 P_2} \\
 V_2 &= \frac{720 \text{ mm} \times 6 \text{ dm}^3 \times 273 \text{ K}}{298 \text{ K} \times 760 \text{ mm}} \\
 V_2 &= 5.2 \text{ dm}^3
 \end{aligned}$$

Example 4.12

Four grams of CH_4 at 27°C and a pressure of 2.5 atm occupies a volume of 2.46 dm^3 . Calculate the value of R .

Solution

$$\text{No of moles of } \text{CH}_4 = \frac{\text{Mass}}{\text{Molecular mass}}$$

$$n = \frac{4}{16} = 0.25 \text{ moles}$$

$$T = 27^\circ\text{C} + 273 = 300 \text{ K}$$

$$P = 2.5 \text{ atm}$$

$$V = 2.46 \text{ dm}^3$$

$$R = ?$$

According to the General Gas Equation,

$$VP = nRT$$

$$\text{or } R = \frac{VP}{nT} \quad \dots\dots\dots (1)$$

$$= \frac{2.46 \text{ dm}^3 \times 2.5 \text{ atm}}{0.25 \text{ mole} \times 300 \text{ K}}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

Example 4.13

Find the density of ammonia gas at 100°C when confined by a pressure of 1600 mm of Hg .

Solution

$$d = ?$$

$$T = 100^{\circ}\text{C} + 273 = 373\text{K}$$

$$P = 1600 \text{ mm of Hg} = \frac{1600}{760} \text{ atm} = 2.105 \text{ atm}$$

$$M_{\text{NH}_3} = 17 \text{ g mole}^{-1}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

Now according to the General Gas Equation,
 $MP = dRT$ (Derived from General Gas Equation)

or $d = \frac{MP}{RT} = \frac{17 \text{ g mole}^{-1} \times 2.105 \text{ atm}}{0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1} \times 373 \text{ K}}$

$$= \frac{17 \times 2.105}{0.0821 \times 373}$$

$$= 1.169 \text{ g dm}^{-3}$$

4.5 DEVIATION FROM IDEAL GAS BEHAVIOUR:

A gas which obeys the general gas equation ($VP = nRT$) and all the gas laws especially Boyle's Law and Charles's Law is called an Ideal gas. No such gas is known. In reality no gas is ideal because they show deviations at low temperature and high pressure. The gases which do not obey general gas equation and all the gas laws strictly are called non-ideal gases. All known gases are found to be real under certain conditions.

The following table shows the volumes of hydrogen gas at different pressures and at constant temperature. Do you think this data verifies Boyle's law?

Pressure (in atm)	Volume (in dm ³)	PV
0.1	224.1	22.41
50	0.4634	23.71
1000	0.384	38.34

The result (PV) is quite different, temperature remains constant.

The real gases show deviation from ideal behaviour at low temperature and high pressure. Van der Waals attributed the deviation of real gases from ideal behaviour due to two **faulty assumptions** in kinetic molecule theory of gases.

- Inter molecular Forces of attraction:**
There are no attractive or repulsive forces between the gas molecules.
- Volume**
The volume of the gas molecules is negligible as compared to the volume of the container.

Explanation of deviations:

- At lower temperature:**
At high temperature the kinetic energy of the gaseous molecules is very high. As a result the attractive forces between them are negligible. But when temperature is

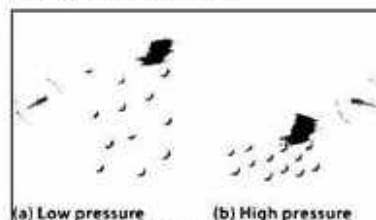


Fig. 4.15: Effect of pressure on volume of one mole of a gas

decreased, the kinetic energy of the molecules decreases. The intermolecular forces become significant. It means that the molecules come close to each other. At a certain very low temperature the gases change into the liquid state. Therefore attractive forces between the gas molecules become significant near liquefying temperature. That is why the ideal gases deviate from their original behaviour at low temperature e.g. SO_2 liquefies at -10°C while H_2 at -252.7°C . Therefore attractive forces between SO_2 molecules cannot be considered negligible at room temperature. For this reason SO_2 gas shows non-ideal behaviour at room temperature as compared to H_2 gas.

(ii) **At high pressure**

At low pressure actual volume of gas molecules is very small as compared to the volume of the container. However, this volume does not remain negligible at high pressure. This can be understood from the following figure.

When pressure is one atm, individual volume of one mole of gas molecules say 32cm^3 is negligible as compared to the total volume of gas 22400cm^3 . But if it is subjected to a pressure of 100atm , the volume of the gas is reduced to 224cm^3 . Under this pressure, individual volume of gas molecules (32cm^3) is not negligible as compared a volume of the gas (224cm^3).

Graphical Representation

For one mole of a gas, if a graph is plotted between $\frac{PV}{RT}$ and pressure, then for an ideal gas, it must give a straight line (the temperature remains at 0°C). But actually it is seen that the gases do not give a straight line. They deviate from their ideal behaviour as shown in the figure.

Actually, when the pressure is initially increased, it pushes the molecules closer and increases the intermolecular forces. Due to these forces, the volume of the gas shrinks more than that predicted from the gas laws. (i.e. Boyle's Law). This will decrease the value of $\frac{PV}{RT}$. That is why the gases do not show a straight line. $\frac{PV}{RT}$ is called **compressibility**

factor. For ideal gases it should be one, whereas for real gases it is not equal to one.

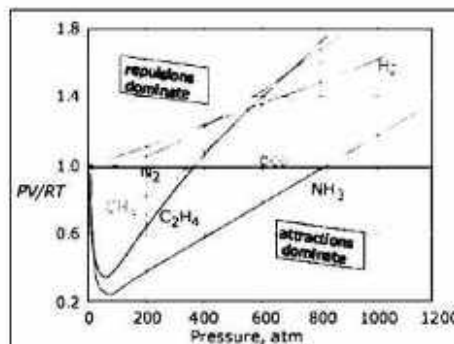


Fig. 4.16: Deviations from ideal behaviour

4.6 VAN DER WAALS EQUATION

(CORRECTION FACTORS TO IDEAL GAS EQUATION)

The general gas equation is not applicable to real gases at all temperatures and pressures. In order to make it applicable to real gases, a Dutch Scientist Van der Waals in 1873 made correction in volume and pressure of the gases and derived an equation known as Van der Waals equation. Both those assumptions are not true at high pressure and low temperature.

Volume Correction

Van der waal thought that, when a gas is compressed the molecules are pushed so close together the repulsive forces operate between them. When pressure is further increased, it is opposed by the molecules themselves. This is because the molecules have definite volume, no doubt very small as compared to the volume of vessel, but it is not negligible. So Vander Waal's postulated that the actual volume of the molecules per mole of gas is represented by b , then the volume available to gas molecules is the volume of vessel minus the volume of gas molecules.

$$V = V_{\text{vessel}} - V_{\text{molecule}}$$

V is free volume

$$V_{\text{molecule}} = nb$$

where b is individual volume of one mole of the gas molecules and ' n ' is total no. of moles of the gas molecules. It is interesting to note that b is not equal to the actual volume of gas. In fact it is four times the actual volume of molecules ($b=4V_m$)

$$\text{So } V = V_{\text{vessel}} - nb \quad \dots\dots\dots (1)$$

Pressure correction

A molecule in the interior of a gas is attracted by other molecules on all sides, so these attractive forces are cancelled out. However, when a molecule is about to strike the walls of the container, it experiences a force of attraction towards the other molecules of the gas, so the molecules cannot hit the walls of the vessels with that much force with which they should have been hitting in the absence of these attractive forces.

It means that the pressure being observed on the walls of the vessels is a little bit lesser than the ideal pressure.

$$\text{Therefore, } P_{\text{observed}} = P_{\text{ideal}} - P_{\text{lessened}}$$

If the ideal pressure is denoted by P and the pressure lessened due to molecular attractions is denoted by P' then

$$P_{\text{observed}} = P - P'$$

$$\text{and } P = P_{\text{observed}} + P'$$

P' is determined by the forces of attraction between molecules which are striking the walls of the container (say type A) and molecules which are pulling them inward (say type B). The net force of attraction is proportional to the concentration of type A and type B molecules.

$$\therefore P' \propto C_A \cdot C_B$$

Let n is the number of moles of A and B type molecules separately and total volume of both types of molecules is V . So,

$$P' \propto \frac{n}{V} \cdot \frac{n}{V} \quad , \quad P' = \frac{an^2}{V^2}$$

$$P' \propto \frac{n^2}{V^2}$$

Where ' a ' is constant of proportionality and is called as co-efficient of attraction per unit volume. It has a constant value for a particular real gas.

$$P = P + \frac{an^2}{V^2}$$

After the correction of volume and pressure, $PV = nRT$ becomes

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

For 1 mole of gas, $n = 1$, then

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

This is the Van der Waals equation for an ideal gas.

Units of 'a'

$$\begin{aligned} \text{As } P &= \frac{n^2 a}{V^2} \text{ or } a = \frac{P V^2}{n^2} \\ &= \frac{\text{atm} \cdot (\text{dm}^3)^2}{\text{mole}^2} \\ &= \text{atm} \cdot \text{dm}^6 \text{ mole}^{-2} \end{aligned}$$

Units of 'b'

As b is incompressible
volume per mole of a gas,
its units should be $\text{dm}^3 \text{ mole}^{-1}$

Van der Waals' Constants for Some Gases

Substance	a ($\text{dm}^6 \text{ atm mole}^{-2}$)	b ($\text{dm}^3 \text{ mole}^{-1}$)
H ₂	0.0247	0.0266
He	0.0034	0.0237
N ₂	0.1408	0.0391
O ₂	0.1378	0.0318
Cl ₂	0.6579	0.0562
Ar	0.1355	0.0322
Kr	0.2349	0.0398
CO	0.1505	0.0399
NO	0.1358	0.0279
CO ₂	0.3640	0.0427
HCl	0.3716	0.0408
SO ₂	0.6803	0.0564
H ₂ O	0.5536	0.0305
NH ₃	0.4225	0.0371
CH ₄	0.2283	0.0428
CCl ₂ F ₂	0.1066	0.0973

Example 4.14

One mole of methane gas is maintained at 300K. Its volume is 250cm^3 . Calculate the pressure exerted by the gas under the following conditions.

- When the gas is ideal
- When the gas is non-ideal, and
 $a = 0.2283 \text{ dm}^6 \text{ atm mole}^{-2}$
 $b = 0.0428 \text{ dm}^3 \text{ mole}^{-1}$

Solution:

- When the gas is ideal
General gas Equation is applied here.
 (a) Gas = Methane:
 $n = 1 \text{ mole}$
 $T = 300\text{K}$
 $V = 250\text{cm}^3 = 0.25\text{dm}^3$
 $R = 0.0821 \text{ dm}^3 \text{ atm Mole}^{-1} \text{K}^{-1}$
 $P = ?$



Now applying the General Gas Equation,

$$PV = nRT,$$

$$P = \frac{nRT}{V}$$

$$= \frac{1 \text{ mole} \times 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.25 \text{ dm}^3}$$

$$= \frac{1 \times 0.0821 \times 300}{0.25} \frac{\cancel{\text{mole}} \times \cancel{\text{dm}^3} \text{ atm } \cancel{\text{mole}^{-1}} \text{ K}^{-1} \times \text{K}}{\cancel{\text{dm}^3}}$$

$$= 98.52 \text{ atm}$$

- (ii) When the gas is non-ideal (Here Van der Waals' equation is applied)

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

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

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Putting the following values in this equation,

$$n = 1 \text{ mole, } R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

$$V = 0.25 \text{ dm}^3, T = 300 \text{ K, } a = 0.2283 \text{ dm}^6 \text{ atm mole}^{-2}, b = 0.0428 \text{ dm}^3 \text{ mole}^{-1}$$

$$P = \frac{1 \text{ mole} \times 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.25 \text{ dm}^3 - (1 \text{ mole} \times 0.0428 \text{ dm}^3 \text{ mole}^{-1})} - \frac{1 \text{ mole}^2 \times 0.2283 \text{ dm}^6 \text{ atm mole}^{-2}}{(0.25 \text{ dm}^3)^2}$$

$$= \frac{24.63 \text{ dm}^3 \text{ atm}}{0.25 \text{ dm}^3 - 0.0428 \text{ dm}^3} - \frac{0.2283 \text{ dm}^6 \text{ atm}}{0.0625 \text{ dm}^6}$$

$$= \frac{24.63 \text{ dm}^3 \text{ atm}}{0.2072 \text{ dm}^3} - 3.6528 \text{ atm}$$

$$= 115.2178 \text{ atm}$$

4.7 DALTON'S LAW OF PARTIAL PRESSURE AND ITS APPLICATIONS

An English Chemist John Dalton (1766-1844) showed in 1801 that “**The total pressure exerted by a gaseous mixture is equal to the sum of partial pressures of each gas present in the mixture.**” The law is only obeyed, if the component gases do not chemically react with each other. Moreover the gases must behave ideally. The partial pressure is the pressure exerted by one component of the gaseous mixture.

$$\text{Total Pressure } (P_t) = P_A + P_B + P_C$$

Whereas P_A , P_B and P_C are the partial pressures of individual gases.

Particular Example

Air is a mixture of non-reacting gases. Percentage of each gas in the gaseous mixture is N_2 (78.08%), O_2 (20%), Ar (0.93%), CO_2 (0.03%). Traces of Ne, He, Kr, H_2 , along with various

amounts of water vapours and pollutant (which can pollute the atmosphere) gases such as oxides of sulphur and Nitrogen are also found in air. The total pressure exerted by the air will be the sum of partial pressure of each gas.

(i) **Relationship between pressure and no. of moles of a gas:**

If n_A , n_B and n_C are the number of moles of the gases and P_A , P_B and P_C be their partial pressures respectively.

Then, according to the general gas equation,

$$PV = nRT$$

$$\text{For gas A, } P_A = \frac{n_A RT}{V} \quad \dots\dots\dots (1)$$

$$\text{For gas B, } P_B = \frac{n_B RT}{V} \quad \dots\dots\dots (2)$$

$$\text{For gas C, } P_C = \frac{n_C RT}{V} \quad \dots\dots\dots (3)$$

$$P_t = \frac{n_t RT}{V} \quad \dots\dots\dots (4)$$

Where n_t (total no. of moles of all the gases) = $n_A + n_B + n_C$

Dividing equation (1) by (4)

$$\frac{P_A}{P_t} = \frac{n_A RT}{V} \div \frac{n_t RT}{V}$$

$$\frac{P_A}{P_t} = \frac{n_A \cancel{RT}}{\cancel{V}} \times \frac{\cancel{V}}{n_t \cancel{RT}}$$

$$\frac{P_A}{P_t} = \frac{n_A}{n_t} \quad P_A = \frac{n_A}{n_t} \times P_t$$

Similarly $P_B \propto n_B$ and $P_C \propto n_C$

In general

$$\text{Partial Pressure of any gas} = \frac{\text{No of moles of that gas}}{\text{Total no of moles of all gases}} \times \text{Total Pressure}$$

(ii) **Relationship between pressure and mole fraction of a gas:**

We know that

$$\frac{\text{Partial Pressure of any gas}}{\text{Total Pressure of all gases}} = \frac{\text{No of moles of that gas}}{\text{Total no of moles of all gases}}$$

$$\frac{P_i}{P_t} = \frac{n_i}{n_t} \text{ or } P_i = \frac{n_i}{n_t} \times P_t$$

but $\frac{n_i}{n_t} = X_i$ where X_i is called mole fraction of the component

$$\text{so, } P_i = P_t X_i$$

Thus the **partial pressure of any component is equal to the product of total pressure of all the components and mole fraction of that component.**

Applications of the Law of Partial Pressure

i. Collection of gases over water:

The Dalton's Law is particularly useful when a gas is generated and subsequently collected over water provided the gas is insoluble in water. The total pressure consists of the pressure of the water vapours in addition to the pressure of the gas that is generated. The pressure due to water vapour is called aqueous tension.

$$\text{Thus } P_{\text{Total}} = P_{\text{gas}} + P_{\text{Water vap}} \quad \text{or} \quad P_{\text{gas}} = P_{\text{Total}} - P_{\text{Water vap}}$$

The gas contaminated with water may be called a moist gas.

ii. Respiration at higher altitudes:

The respiration process in living things depends upon the differences in partial pressure e.g. partial pressure of O_2 in the outside air is higher (159 mmHg) than in the lungs where the partial pressure of O_2 is lower (116 mmHg). However at high altitudes, the pressure of oxygen decreases and the pilots may have un-comfortable breathing in a non-pressurized cabin where the partial pressure of O_2 is about 150 mmHg.

iii. Respiration by deep sea divers:

Deep sea divers breathe air under increased pressure. At a depth of 40 metres, the pressure increases 5 times than the normal pressure. Therefore regular air cannot be used in diver's tanks because the partial pressure of O_2 would be 795 mm of Hg ($159 \times 5 = 795$ mm of Hg) in that case. Therefore deep sea divers use to breathe a mixture of 96% He and 4% O_2 (Heliox) in the respiration tank, the scuba.

A scuba (self-contained breathing apparatus having oxygen used by divers underwater) contains compressed air to breath. As diver returns to the surface, it becomes hazardous for him if not handled properly. As the diver comes up, the pressure of the surrounding water drops. Consequently, the compressed air in the lungs expands. Surfacing must be done very slowly so that the compressed air may escape out from the lungs without causing damage to them.

iv. How deep sea divers respire on return from sea:

The percentage of N_2 in air is about 80%. If N_2 is present in diver's tank, the solubility of N_2 in blood can increase with increase in pressure in very deep sea. And blood of a diver may be saturated with N_2 during a dive. If the diver returns quickly and relatively at low pressure at the surface, he will face life threatening condition called the "bends". Deep sea divers must either use different solutions of gases such as He in O_2 or spend many hours in a decompression chamber after a dive. The pressure in a decompression chamber is slowly lowered over many hours. Nitrogen gas comes out of the blood and disposed off safely for normal breathing.

DO YOU KNOW

The mixture of oxygen and helium used in sea diver's tanks is called heliox. It is also used in hospital to facilitate patients suffering from Asthma.

Example 4.15

At 27°C a volume of 500cm^3 of H_2 measured under a pressure of 400 mm of Hg and 1000cm^3 of N_2 measured under a pressure of 600 mm of Hg are introduced into an evacuated 2dm^3 flask. Calculate the resulting pressure.

Solution

We will apply Boyle's Law, as the temperature is constant.

For H_2

$$V_1 = 500 \text{ cm}^3 = \frac{500}{1000} = 0.5 \text{ dm}^3$$

$$V_2 = 2 \text{ dm}^3$$

$$P_1 = 400 \text{ mm Hg}$$

$$P_2 = ?$$

According to Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{400 \text{ mm Hg} \times 0.5 \text{ dm}^3}{2 \text{ dm}^3} \\ = 100 \text{ mm Hg}$$

For N_2

$$V_1 = 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

$$V_2 = 2 \text{ dm}^3$$

$$P_1 = 600 \text{ mm Hg}$$

$$P_2 = ?$$

According to Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{600 \text{ mm of Hg} \times 1 \text{ dm}^3}{2 \text{ dm}^3} \\ = 300 \text{ mm Hg}$$

$$\begin{aligned} \text{Hence Total Pressure} &= p_{\text{H}_2} + p_{\text{N}_2} \\ &= 100 \text{ mm Hg} + 300 \text{ mm Hg} \\ &= 400 \text{ mm Hg} \end{aligned}$$

Example 4.16

Find the total pressure exerted by 2g of ethane and 3g of CO_2 contained in a 5 dm^3 vessel at 50°C .

Solution

$$44 \text{ g of } \text{CO}_2 = 1 \text{ mole}$$

$$3 \text{ g } \text{CO}_2 = \frac{1}{44} \times 3 = 0.068 \text{ mole}$$

$$\text{Number of moles of } \text{CO}_2 = 0.068 \text{ mole}$$

$$V = 5 \text{ dm}^3 \quad T = 50^\circ\text{C} + 273 = 323 \text{ K} \quad R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$$

Now according to the General Gas Equation

$$PV = nRT \text{ or } P_{\text{CO}_2} V = n_{\text{CO}_2} RT \quad \text{or} \quad P_{\text{CO}_2} = \frac{n_{\text{CO}_2} RT}{V}$$

$$P_{\text{CO}_2} = \frac{0.068 \text{ mole} \times 0.0821 \times \text{dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1} \times 323 \text{ K}}{5 \text{ dm}^3}$$

$$= \frac{0.068 \times 0.0821 \times 323}{5} = 0.361 \text{ atm}$$

$$30 \text{ g Ethane (C}_2\text{H}_6) = 1 \text{ mole}$$

$$2 \text{ g Ethane (C}_2\text{H}_6) = \frac{1}{30} \times 2 = 0.067 \text{ mole}$$

$$V = 5 \text{ dm}^3 \quad n = 0.067 \text{ moles} \quad T = 50^\circ\text{C} + 273 = 323 \text{ K}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1}$$

$$PV = nRT \quad \text{or}$$

$$P_{\text{C}_2\text{H}_6} = \frac{n_{\text{C}_2\text{H}_6} RT}{V}$$

$$P = \frac{nRT}{V} = \frac{0.067 \text{ moles} \times 0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1} \times 323 \text{ K}}{5 \text{ dm}^3} = 0.355 \text{ atm}$$

$$\begin{aligned} \text{Total Pressure} &= P_{\text{CO}_2} + P_{\text{C}_2\text{H}_6} \\ &= 0.361 \text{ atm} + 0.355 \text{ atm} \\ &= 0.716 \text{ atm.} \end{aligned}$$

Example 4.17

1.00 mole of N_2 and 3.00 moles of H_2 are enclosed in a container of volume 10.0 dm^3 at 298 K . What are the partial pressures and the total pressure?

Solution

$$\text{No of moles of } \text{N}_2 (n_1) = 1.00 \text{ mole}$$

$$\text{No of moles of } \text{H}_2 (n_2) = 3.00 \text{ mole}$$

$$\text{Total number of moles (n}_{\text{Total}}) = 1 + 3 = 4 \text{ mole}$$

$$V = 10.0 \text{ dm}^3$$

$$T = 298 \text{ K}, R = 0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1}$$

According to the General Gas Equation, $PV = nRT$

$$\begin{aligned} \text{or } P_{\text{Total}} &= \frac{n_{\text{Total}} RT}{V} = \frac{4 \times 0.0821 \times 298}{10} \cdot \frac{\text{dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1} \times \text{K}}{\text{dm}^3 \text{ mole}^{-1}} \\ &= \frac{4 \times 0.0821 \times 298}{10} \text{ atm} \\ &= 9.77 \text{ atm} \end{aligned}$$

$$P_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{Total}}} \times P_{\text{Total}} = \frac{1}{4} \times 9.77 = 2.44 \text{ atm}$$

$$P_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{Total}}} \times P_{\text{Total}} = \frac{3}{4} \times 9.77 = 7.33 \text{ atm}$$

Example 4-13

A certain mass of H_2 gas collected over water at $6^\circ C$ and 765 mm Hg pressure occupied a volume of 35cm^3 .

Calculate its dry volume at S.T.P. (V.P. of water at $6^\circ C = 7\text{mm of Hg}$)

Solution:

$$V_1 = 35\text{cm}^3, \quad V_2 = ? \quad P_1 = 765 - 7\text{mmHg} = 758\text{mmHg} \quad P_2 = 760\text{mmHg} \\ T_1 = 6 + 273 = 279\text{K}, \quad T_2 = 273\text{K}$$

Applying the Gas Equation,

$$\frac{V_1 P_1}{T_1} = \frac{V_2 P_2}{T_2} \quad \text{or} \quad V_2 = \frac{V_1 P_1 T_2}{T_1 P_2} = \frac{35\text{cm}^3 \times 758\text{mmHg} \times 273\text{K}}{279\text{K} \times 760\text{mmHg}} = 34.2\text{cm}^3$$

**Self Check Exercise 4.6**

A gas was collected over water at $10^\circ C$ and 803mm of Hg. If the gas occupies 73cm^3 , calculate the volume of dry gas at S.T.P. (aqueous tension at $10^\circ C = 9.2\text{mmHg}$).

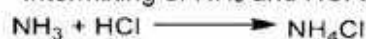
(Ans: = 73.55cm^3)

Diffusion:

The spontaneous intermixing of molecules of one gas with another at a given temperature and pressure is called Diffusion. **Diffusion** is the random movement of a gas from an area of higher concentration to an area of lower concentration.

e.g. (i) Fragrance of rose.

(ii) Intermixing of NH_3 and HCl to gives dense white fumes of NH_4Cl .



(iii) Reddish brown bromine (Br_2) gas taken in a test tube will combine with air taken in another test tube. Red colouration of Br_2 gas will spread in the test tube containing air.

(iv) If liquid ink is left in the bottom of test tube containing water, it will spread evenly throughout the water.

Effusion

The movement of gaseous molecules through extremely small pores in a region of low pressure is called Effusion. This escaping of molecules is not due to collisions but due to their tendency to escape one by one.

4.8 GRAHAM'S LAW OF DIFFUSION AND EFFUSION

An English Scientist, Thomas Graham in 1831 (1805-1869), measured the rates at which equal volumes of various gases escaped from an apparatus at the same temperature and pressure. Graham found that the less dense a gas was (the lighter its particles), the faster the gas escaped.

Graham's Law of diffusion and effusion of gases:

In 1831 Graham showed that "**Rate of diffusion or effusion of a gas is inversely proportional to the square root of its density**". Later in 1848 he himself showed that "**The rate of diffusion or effusion of a gas is inversely proportional to the square root of its molar mass.**"

Mathematically it can be shown as

$$r \propto \frac{1}{\sqrt{d}} \quad \text{(i)} \quad \text{and} \quad r \propto \frac{1}{\sqrt{M}} \quad \text{.....(ii)}$$

where r = rate of diffusion,
 d = density of the gas, and M = Molar mass of the gas

From equation (i) $r \propto \frac{1}{\sqrt{d}}$ or $r = k \times \frac{1}{\sqrt{d}}$ (iii)

and from equation (ii) $r \propto \frac{1}{\sqrt{M}}$ or $r = k \frac{1}{\sqrt{M}}$ (iv)

where k = constant of proportionality.

Let us have two gases with r_1 and r_2 as their rates of diffusion and d_1, d_2, M_1, M_2 be their densities and molar masses respectively.

For two different gases, equation (iii) can be written as

$$r_1 = \frac{k}{\sqrt{d_1}} \quad \text{.....(v)} \quad \text{and} \quad r_2 = \frac{k}{\sqrt{d_2}} \quad \text{.....(vi)}$$

Dividing equation (v) by (vi),

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{and may also be written as} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{because } d \propto M$$

$$\text{Thus} \quad \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Example 4.19

Equal volumes of HCl and SO_2 are confined in a porous container. What would be the comparative rates of diffusion of these gases through the porous walls? The molecular masses of HCl and SO_2 are 36.5 and 64 respectively.

Solution

Molecular mass of HCl (M_1) = 36.5 amu

Molecular mass of SO_2 (M_2) = 64 amu

Rate of diffusion of HCl (r_1) = ?

Rate of diffusion of SO_2 (r_2) = ?

According to the Graham's Law of Diffusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{64}{36.5}}$$

$$r_1(\text{HCl}) : r_2(\text{SO}_2)$$

$$1.33 : 1$$

Hence rate of diffusion of HCl will be 1.33 times the rate of diffusion of SO_2 .



Self Check Exercise 4.7

If 465cm^3 of SO_2 can diffuse through porous partition in 30 seconds. How long will 620 cm^3 of H_2S take to diffuse through the same partition (H = 1, S = 32, O = 16)

(Ans: 29.15 sec)

4.9 LIQUEFACTION OF GASES

Principle

The gases can be liquefied by **Joule-Thomson's effect**. The liquefaction of a gas requires high pressure and low temperature. When a highly compressed gas is allowed to escape out through a throttle (small hole), the temperature falls to such an extent that it changes into the liquid form.

At high pressure, the gaseous molecules come close to each other with the result that the molecular attractions increase. When it is allowed to escape through a nozzle (small hole) into a region of low pressure, the molecules move apart. In doing so, energy is needed to overcome the intermolecular attractions. This energy is taken from the molecules themselves. Therefore the gas is cooled. This process is repeated for many times until the gas completely changes into the liquid form.

Working Steps of Linde's Method

According to Joule-Thomson's effect **"When a highly compressed gas is allowed to escape out through a throttle the temperature of the gas falls to such an extent, that it changes into the liquid form"**. This is the basic principle of the adiabatic expansion which is thermally isolated from its environment.

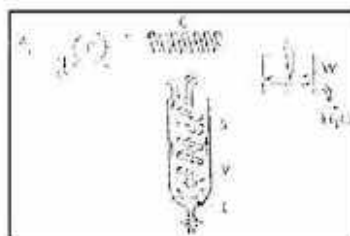


Figure 4.19: Linde's method for liquefaction of air

Working Steps

- Air is compressed to 200 atm approx.
- Most of the water in the air condenses and is removed.
- The heat generated as a result of compression is removed by passing the gas through coils C. (Figure 4.19)
- The dry gas is then passed through a copper spiral coil S.
- It is then expanded to almost atmospheric pressure through a controlled valve V.
- When the air comes out of the valve the expansion takes place from 200atm to 1atm. In this way fall of temperature occurs. This cold air goes up and cools the incoming compressed air.
- The cycle is repeated several times.
- The temperature of the expanding gas finally drops and the remaining air is liquefied.
- The liquid air collects in the chamber L and can be drawn off.
- Any uncondensed air is re-circulated.

Uses of Linde's Method

i. Construction of appliances

The construction of appliances such as refrigerators, heat pumps and air conditioners all work on the principle of Joule-Thomson's effect.

In a refrigerator a compressor compresses a gas such as Freon.

Thus an increase in temperature takes place. The hot Freon gas moves to a condenser on the outside of the refrigerator. Air at room temperature cools the gas down and as a result condenses into liquid.

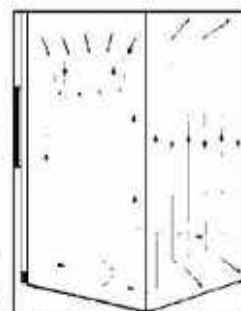


Figure 4.20 Cooling gas path in a refrigerator

The liquid Freon, now at room temperature, is then passed through a small hole in a restriction valve into the low pressure tubes which are inside the refrigerator. There, the Freon liquid vaporises rapidly. The heat of vaporisation needed to do this is drawn from the kinetic energy of the Freon molecules becoming very cold. This cold gas absorbs heat from the refrigerator and its contents, thereby cooling. Then the Freon gas is once again fed into the compressor and the cycle starts over again.

ii. Self cooling pop can (container)

A small container holding liquid CO_2 is built right into the can. When the can is opened, the liquid CO_2 vaporises and escapes out of the top of the can. The heat absorbed by the vaporising CO_2 can lower the temperature of the POP by about 16°C in a few seconds. Thus the temperature is lowered considerably.



Figure 4.21

Applications of Kinetic Molecular Theory

i. Velocity of molecules:

The equation for the root mean square velocity deduced from kinetic equation is

$$C_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

C_{rms} = root mean square velocity

M = molecular mass of the gas

T = absolute temperature.

This equation gives a quantitative relationship between the absolute temperature and the velocities of gas molecules. Higher the temperature of a gas, greater would be the velocities of the molecules.

ii. Graham's Law of diffusion of gases:

According to the postulates of Kinetic Molecular Theory, the Kinetic Energy of the particles is proportional to the Absolute Temperature.

$$\text{As, } E_k = \frac{1}{2}mv^2 \Rightarrow \frac{2E_k}{m} = v^2 \Rightarrow v = \sqrt{\frac{2E_k}{m}} \Rightarrow v = \sqrt{\frac{1}{m}} \sqrt{2E_k}$$

as at constant temperature K.E will remain constant so $\sqrt{2E_k} = \text{Constant}$

$$\text{Therefore } v \propto \sqrt{\frac{1}{m}}$$

Thus the kinetic molecular theory predicts that the average speed depends upon the molecular mass (m). Further the average speed of the particles is inversely proportional to the square root of their molecular mass.



Self Check Exercise 4.8

1. A person can inhale a maximum of 0.115 moles of air per breath. Calculate the maximum volume of air, a person can inhale in one breath if the atmospheric pressure is 100kPa and the person's body temperature is 37°C . (Ans: 2.96 dm^3)
2. 130 cm^3 of a gas exerts a pressure of 750 mm of Hg at 20°C . Calculate its pressure if its volume is increased to 150 cm^3 at 35°C . (Ans: 683.28 mm)

4.10 FOURTH STATE OF MATTER – THE PLASMA

Plasma is the fourth state of matter. It was identified by William Crooks in 1879. He obtained it by heating molecular gas changing into atomic form and then to ionic form at higher temperature. (Molecular gas $\rightarrow$ Atomic gas $\rightarrow$ Ions)

At a higher temperature of 10000K to 100000K (10eV to 100eV) electrons are removed from the atoms to form ions. Plasma is composed of a mixture of un-ionized gas, free electrons and positively charged particles. Most of the universe contains matter in the Plasma state (about 99%). All shining stars and interstellar space is filled with plasma. On our planet earth, plasma does not exist. Plasma is fourth state of matter because of unique physical properties, distinct from solids, liquids and gases.

DO YOU KNOW

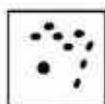
Black holes which are not directly visible are thought to be fuelled by accreting ionizing matter i.e. plasma

It is a substance in which many of the atoms or molecules are ionised effectively allowing charges to flow freely. It takes place at very high temperature. Plasma has the following properties:

- Plasma consists of neutral particles, positive ions and free electrons.
- Plasma is strongly influenced by both magnetic and electric force.
- Plasma shows a characteristic glow depending upon the gas present in the discharge tube e.g. oxygen gives a red glow, hydrogen green and Nitrogen purple or pink glow.

References for additional information

- Thomas J. Green Bowe, Jeffrey Pribyl and K. A. Burke, Chemistry an Experimental Science.
- Graham Hill and John Holmar, Chemistry in context.
- John C. Kotz, Paul M. Treichel and Gabriela C. Weaver, Chemistry and chemical reactivity.



1. Choose the correct answer (MCQs)

- When compressed hydrogen is allowed to expand rapidly, it causes;
(a) Cooling (b) Heating (c) Liquefaction (d) Solidification
- 760 torr is equal to _____ Pascal.
(a) 760 Pascal (b) 101325 Pascal (c) 1.01325 Pascal (d) One Pascal.
- The number of molecules in 4 g H_2 are _____ number of molecules of 56 g of N_2 .
(a) Equal to (b) less than (c) Greater than (d) None of these.
- According to the Kinetic theory of gases, the molecular collisions are elastic. Such collisions cause;
(a) No energy change (b) A small energy change
(c) High energy change (d) None of these.
- What volume would one mole of hydrogen occupy at S.T.P?
(a) 11.2 dm³ (b) 22.4dm³ (c) 33.6dm³ (d) 44dm³

- vi. According to Graham's Law of diffusion, the rate of diffusion of H_2 and O_2 has the ratio;
 (a) 1:4 (b) $1:\sqrt{4}$ (c) 4:1 (d) 2:32.
- vii. Deep sea diver's tank contains;
 (a) 96% He + 4% O_2 (b) 4% N_2 + 96% O_2
 (c) 50% N_2 + 50% O_2 (d) None of these
- viii. In S.I units, the value of R is;
 (a) $8.3413 \text{ Nm K}^{-1} \text{ mole}^{-1}$ (b) $8.3143 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$
 (c) $0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$ (d) None of these
- ix. According to Kinetic Molecular theory kinetic energy of molecules increases when they;
 (a) Are mixed with other molecules at low temperature
 (b) Are frozen into solid (c) Are condensed into liquid
 (d) Are melted from solid to liquid state.
- x. Which gas is more ideal at S.T.P.?
 (a) SO_2 (b) H_2S (c) NH_3 (d) H_2
- xi. On heating direct conversion of a solid in to gas is called;
 (a) evaporation (b) sublimation (c) diffusion (d) boiling
- xii. In which of the following are the particles the most disordered?
 (a) water (b) steam at 100°C (c) impure water at 102°C (d) water at 0°C
- xiii. When steam condenses, the particles;
 (a) shrink to a smaller size (b) lose energy to their surroundings
 (c) move further apart (a) vibrate about fixed positions.
- xiv. The particles of a gas can be described as;
 (a) only moving outwards in direction (b) vibrating about defined position
 (c) rising upwards (d) moving randomly in all directions.
- xv. Which of these changes would speed up the rate of diffusion the most?

Change	Temperature	Pressure
a	Decrease	Decrease
b	Decrease	Increase
c	Increase	Increase
d	Increase	Decrease

- xvi. Which of the following gas has the lowest density under room conditions?
 (a) CO (b) N_2 (c) Ne (d) NH_3 (e) O_2
- xvii. Which statement provides the best evidence that matter may exist as tiny particles moving at "random motion"?
 (a) Many elements conduct electricity.
 (b) Air can be readily compressed.
 (c) A small mass of water produces a much larger volume of steam.
 (d) If a bottle of ether is opened, the smell is quickly detected in all parts of the room.

- xviii. Which of the following is an example of diffusion?
- Bubbles rising in a beaker of boiling water.
 - Steam condensing on a cold window.
 - Water spreading out on the surface of a table.
 - The spreading of the smell of flowers in a garden.
- xix. Which statement explains why the compounds propane and CO_2 diffuse at the same rate?
- They are both gases.
 - Their molecules contain carbon.
 - They have the same relative molecular mass.
 - Both are denser than air.

2 Write brief answers to the following:

- What is Absolute Zero and Absolute Scale of temperature?
 - What is Plasma?
 - What are the different units of gas constant (R)?
 - Define Pressure. How will you explain its different units?
 - Define Charles Law. How will you derive Absolute Zero with its help?
 - Define Avogadro's Law.
 - What is the difference between an ideal gas and a real gas?
 - How will you derive the general gas equation with the help of Boyle's law and Charles's law?
- 3** What are the main postulates of the Kinetic Molecular theory of gases?
- 4** Relate temperature to the average K.E of the particles in a substance.
- 5** (a) What are the Standard Temperature and Pressure? (S.T.P).
 (b) What is the density in grams per dm^3 of SO_2 at 25°C and 300 mm of Hg pressure?
- 6** (a) Kinetically how will you interpret the effect of temperature on gaseous molecules?
 (b) How will you explain the gas pressure with the help of Kinetic Theory?
- 7** (a) Define pressure. Derive SI units unit of pressure.
 (b) Explain the effect of change in pressure on the volume of a gas, temperature remains constant. — Boyle's Law.
 (c) How will you verify it graphically?
 (d) A sample of air occupies 1 dm^3 at room temperature and pressure. What pressure is needed to compress it so that it occupies only 100 cm^3 at that temperature?
(Ans: 10atm)
- 8** How will you explain the effect of change in temperature on the volume of the gas?
 (a) Give a graphic representation of the Charles's Law.
 (b) To what temperature must a 1 dm^3 sample of a perfect gas be cooled from room temperature in order to reduce its volume to 100 cm^3 ?
(Ans: 29.8k)
- 9** (a) How will you derive the Absolute Zero?
 (b) How will you explain the Absolute Temperature scale on the basis of Charles Law?
- 10** (a) Define and Explain Avogadro's Law, How does it help to determine
 (i) Mass (ii) Volume (iii) Molecules of the gas
 (b) Can we derive the Avogadro's Law for liquids and solids?

- 11 (a) How will you derive the Ideal or General Gas Equation with the help of Boyle's Law, Charles Law and Avogadro's Law?
 (b) How will you determine
 - (i) Molecular mass of the gas.
 - (ii) Density of the gas by Ideal Gas Equation.
- 12 (a) The value of Ideal Gas constant (R) can be calculated in three ways. Explain these three ways in detail.
 (b) The density of air at 161.325 kPa and 298.15K is 1.59g dm⁻³. Assuming that the air behaves as an ideal gas, calculate its molar mass. (Ans: 22.48g mole⁻¹)
- 13 (a) What is the difference between a real gas and an Ideal or perfect gas. What are the deviations in Ideal behaviour of real gases?
 (b) What are the causes of deviations of real gases from their ideal behaviour. Explain these deviations at
 - (i) Low temperature.
 - (ii) High pressure.
- 14 How will you derive the Van der Waal's Equation keeping in view the general or ideal gas equation ($VP = nRT$).
- 15 (a) Define and explain the Dalton's law of partial pressure. How does it explain the
 - (i) Relationship between pressure and mole of a gas
 - (ii) Relationship between pressure and mole fraction of component.
 (b) Give practical applications of the Dalton's law of partial pressure.
- 16 (a) By use of the Van der Waal's equation, find the temperature at which 3 moles of SO₂ will occupy a volume of 10 dm³ at a pressure of 15 atm.
 $a = 0.6803 \text{ atm dm}^6 \text{ mole}^{-2}$, $b = 0.0564 \text{ dm}^3 \text{ mole}^{-1}$ (Ans: 336.43°C)
 (b) A certain gas occupies a volume of 6 dm³ under a pressure of 720 mm of Hg at 25°C. What volume will this gas occupy under standard conditions? (Ans: 5.2 dm³)
- 17 (a) Define and derive the Graham's law of effusion and diffusion.
 (b) The time required for a given volume of N₂ to diffuse through an orifice is 35 seconds. Calculate the molecular weight of a gas which requires 50 sec to diffuse through the same orifice under identical conditions. (Ans: 13.72 g/mol)
- 18 (a) Interpret phenomenon liquefaction of gases.
 (b) How will you liquefy gases by Linde's method?



5

LIQUIDS



After completing this lesson, you will be able to:

This is 9 days lesson
(period including homework)

- Define molar heat of fusion and molar heat of vaporization.
- Define dynamic equilibrium between two physical states
- Describe simple properties of liquids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on Kinetic Molecular Theory.
- Explain physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension.
- Describe how heat of fusion and heat of vaporization affect the particles that make up matter.
- Explain applications of dipole-dipole forces, hydrogen bonding and London forces
- Use the concept of Hydrogen bonding to explain the following properties of water: high surface tension, high specific heat, low vapour pressure, high heat of vaporization, and high boiling point. And anomalous behaviour of water when its density shows maximum at 4 degree centigrade.
- Relate energy changes with changes in intermolecular forces.
- Describe liquid crystals and give their uses in daily life.
- Differentiate liquid crystals from pure liquids and crystalline solids.

INTRODUCTION

A simple definition of a liquid is that "it is a material that assumes the shape of a container without filling it completely". A gas on the other hand takes the shape of the vessel and has the characteristics to fill it completely. A solid neither takes the shape of the vessel nor fills the container completely. The definition of a liquid is satisfactory on the whole with the exception of glasses, polymers (e.g. PVC etc); they appear in the solid but at higher temperatures they behave like liquid even before they melt. The cohesive force i.e. force of attraction between molecules of substance in a liquid are stronger than those in a gas even at high pressure.

5.1 KINETIC MOLECULAR INTERPRETATION OF LIQUIDS

The kinetic molecular theory also applies to liquids. Postulates of kinetic molecular theory of liquids are given below:

- (a) A liquid is made up of molecules which touch one another.

- (b) The molecules within the liquid are in constant motion but the movement of molecules is restricted due to their close packing together.
- (c) Attractive forces among liquid molecules are greater than those among gas molecules. However these attractive forces are not sufficient to hold molecules in fixed position. The liquid molecules can slide each other.
- (d) The average Kinetic Energy of liquid molecules is directly proportional to the Absolute Temperature.
- (e) At constant temperature, the average K.E of the molecules is equal to the K.E of the vapours of liquids.

Simple Properties of Liquids

There are some simple properties of liquid e.g. diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces, and Kinetic Energy based on Kinetic Molecular Theory. We can use the Kinetic Molecular Theory to account for the simple properties of liquids.

i. Diffusion

The diffusion in liquids takes place because the molecules move from one place to another due to K.E. The restricted movement of the molecule reduces the rate of diffusion e.g. a drop of ink when added to water diffuses slowly due to relatively small empty spaces between the molecules. The diffusion between closely packed molecules of liquids is slow due to less collision between them.

ii. Compression (effect of pressure)

A liquid cannot be compressed significantly by increasing the pressure because the molecules are already in close contact with one another e.g. an increase of pressure from one to two atmospheres reduces the volume of water to 0.0045 percent which is negligible. However the same pressure reduces the volume of a gas up to 50 percent.

iii. Expansion (effect of temperature)

The liquids expand on heating because the intermolecular forces between them decrease. Moreover the increase of temperature increases the effective collisions between the molecules. If the temperature is decreased, contraction of volume takes place. This property is useful for making thermometers, e.g. mercury thermometer. In it, if the temperature rises, the mercury expands in the capillary tube. As the volume of capillary is much less than the volume of the bulb containing mercury, a small expansion gives a large movement of mercury thread.

iv. Motion of molecules

The molecules move with lesser speed due to larger forces of attraction among them, As a result they have lesser kinetic energy. However the kinetic energy increases with the increase of temperature.

v. Spaces between them

The molecules forming the liquid states are fairly close to each other. There is very little



space between them. As a result the numbers of collisions among the molecules are moderate. Therefore, the average kinetic energy is also moderate.

vi. **Intermolecular forces**

The attractive forces existing between the individual particles of a substance are called intermolecular forces. The physical properties of liquids such as boiling point, vapour pressure, surface tension, viscosity and heat of vaporization depend upon the strength of intermolecular attractive forces.

vii. **Kinetic Energy based on Kinetic Molecular Theory**

According to the kinetic molecular theory, the molecules due to strong inter-molecular attractions have minimum movements and minimum collisions. Let us consider the example of water, as the molecules are closer to each other and have strong forces of attractions due to hydrogen bonding so have low kinetic energy.

5.2 INTERMOLECULAR FORCES

The forces of attractions among the molecules of a liquid are called inter-molecular forces. For example, water exists as a liquid due to inter-molecular attractions called hydrogen bonds. The forces of attraction existing

between the molecules of a substance are also known as Vander Waal's forces. The physical properties of liquids can be explained in terms of their intermolecular forces.

DO YOU KNOW

Lizards can stick to walls and ceilings because of Vander Waal's forces.

The intermolecular forces are of five types:

- Dipole-Dipole forces
- Ion-Dipole forces
- Dipole-induced dipole forces
- London Dispersion forces
- Hydrogen bonding

5.2.1 Dipole-Dipole Forces

Polar molecules have charges at different parts of a molecule. Due to these charges they attract each other.

The attractive forces between the positive ends of one molecule with the negative end of other molecule are called dipole – dipole forces. This means dipole – dipole interactions are electrostatic interactions between permanent dipoles in molecules. Examples of polar molecules include hydrogen chloride (HCl) chloroform (CHCl_3) etc.

Stronger these dipole-dipole forces, greater would be the value of thermodynamic parameters like melting point, boiling point, heat of vaporization, heat of sublimation etc.

5.2.2 London Dispersion Forces

The forces of attractions between non-polar molecules which become polar for an instant are called London dispersion forces.

Substances like hydrogen, helium, neon, argon, chlorine, fluorine, methane etc are non-

polar in nature. These gases can be liquefied and solidified under appropriate conditions. Some forces must be holding these molecules in contact with one another in the liquid and solid states.

In He gas, on the average, the electron charge density is evenly distributed in a spherical region about the nucleus. However, at any given instant, the actual location of two electrons relative to the nucleus can produce an instantaneous dipole. This temporary dipole, in turn, can influence the distribution of electrons in neighbouring helium atoms, producing induced dipoles in those atoms (Fig. 5.1).



Fig. 5.1: London dispersion forces Instantaneous dipole

The forces of attraction between an instantaneous dipole and an induced dipole are known as a dispersion force. It is also called as London dispersion force, named for Fritz London who offered a theoretical explanation for these forces in 1928.

Factors Affecting London Dispersion Forces

Factors affecting the London dispersion force are:

- Atomic or molecular size
- Polarizability
- Number of atoms in a molecules

(i) Atomic or Molecular Size

The strength of these forces depends upon the size of the electronic cloud of the atom or molecule. With the increase in size of atom or molecule, the dispersion becomes easy and these forces become prominent. Inert gases are all monoatomic gases. They do not make covalent bonds with other atoms because their valence shells are complete. Their boiling point increase down the group from He to Rn (Table 5.1). This is because of increase in molecular size.

Table 5.1: Boiling points of noble gasses

Noble Gas	He	Ne	Ar	Kr	Xe	Rn
Boiling Points (°C)	-268.6	-245.9	-185.7	-152.3	-107.1	-61.8

(ii) Polarizability

The polarizability of an atom or molecule is a measure of the ease with which electron charge density is distorted. Large atoms have more electrons and larger electron cloud than small atoms. In large atoms, the outer electrons are more loosely bound, they can shift

towards another atom more easily than the more tightly bonded electrons in small atoms. This means polarizability increases with increased atomic and molecular size. For example among halogens, the first member, F_2 is a gas at room temperature, the second member, Cl_2 is also a gas but it is more easily liquefied than F_2 . Bromine is a liquid and Iodine is solid at room temperature. Because large molecules are easily polarizable, the intermolecular forces between them are strong enough to form liquids or solids.

(iii) Number of atoms in a molecule

Elongated molecules make contact with neighbouring molecules over a greater surface than do small molecules. Greater the number of atoms in a molecule, greater is the polarizability of the molecule. Table 5.2 shows boiling points and physical states of some hydrocarbons.

Table 5.2: Boiling points and physical states of some hydrocarbons.

Molecular formula	B.P ($^{\circ}C$ at 1 atm)	Physical State at STP
CH_4	-161.5	Gas
C_2H_6	-88.6	Gas
C_3H_8	-42.1	Gas
C_4H_{10}	-0.5	Gas
C_5H_{12}	36.1	Liquid
C_6H_{14}	68.7	Liquid
$C_{10}H_{22}$	174.1	Liquid

Note that C_2H_6 and C_6H_{14} have the boiling points as $-88.6^{\circ}C$ and $68.7^{\circ}C$ respectively. This shows that the molecule with a large chain length experiences stronger attractive forces.

5.2.2 Hydrogen Bonding

A hydrogen bond is the attraction between the lone pair of an electronegative atom and a hydrogen atom that is bonded to either N, O or F. This limits hydrogen bonding mainly to the participation of nitrogen, oxygen and fluorine atoms. Hydrogen bonds are weaker than covalent bonds but stronger than dipole-dipole interactions, which are stronger than London dispersion forces. The boiling point and heat of vaporization of water are higher than those of H_2S because H_2O molecules attract each other through H-bonding whereas H_2S molecules attract each other by dipole-dipole interactions.

Applications of Hydrogen Bonding

(i) Thermodynamic properties

The boiling points of hydrides of group IVA, VA, VIA and VIIA plotted against period number of the periodic table is shown in figure 5.2.

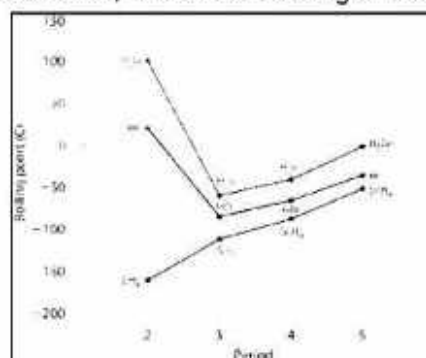


Fig. 5.2: A graph between period number and the boiling points of hydrides

The boiling point of hydrides

Note that hydrides of group IVA have lower boiling points. The reason is that these hydrides are non-polar and have only London dispersion forces among their molecules. Hydrides of group VA, VIA and VII-A have polar molecules. NH_3 , H_2O and HF show maximum boiling points in their respective series. This is due to hydrogen bonding in their molecules. The boiling point of H_2O seems to be more affected than that of HF . As F is more electronegative than O. One should expect H-bonding to be stronger in HF than H_2O . But boiling point of H_2O is higher than that of HF . The reason is that fluorine can make only one hydrogen bond with hydrogen of the neighbouring molecule. On the other hand oxygen atom can form two hydrogen bonds with the neighbouring molecules. NH_3 can also form only one hydrogen bond per molecule as it has only one lone pair.

(ii) Solubility of Hydrogen Bonded Molecules

The compounds that have hydrogen bonds are soluble in each other. Ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other. Similarly carboxylic acids are also soluble in water, if their molecular sizes are small.

(iii) Cleansing Action

Soaps and detergents perform the cleaning action. Their molecules contain both polar and non-polar ends. Their polar parts are water soluble due to hydrogen bonding and non-polar part dissolve oil or grease. Attraction between water and polar end of soap molecule carries the oil or grease droplet into the water.

(iv) Hydrogen Bonding in Paints and Dyes

Paints and dyes have adhesive action due to hydrogen bonding. Similarly hydrogen bonding also makes glue and honey sticky substances.

(v) Clothing

We use cotton, silk or synthetic fibres for clothing. Hydrogen bonding is of great importance in thread making materials. This hydrogen bonding is responsible in their rigidity and tensile strength.

(vi) Food Materials

Food materials like carbohydrates consist of glucose, fructose, sucrose, each of them contains $-\text{OH}$ groups which is responsible for H-bonding in them.

(vii) Hydrogen Bonding in Biological Molecules

The structure of proteins, substances essential to life, is determined partly by hydrogen bonding. The action of enzymes, the protein molecules that catalyze the reactions that sustain life, depends in part on the forming and breaking of hydrogen bonds. The hereditary information passed from one generation to the next is carried in nucleic acid molecules joined by hydrogen bonds into an elegant structure.

5.3 PHYSICAL PROPERTIES OF LIQUIDS

In a liquid the molecules are very close to each other due to the presence of intermolecular forces. As a result their independent motion is greatly hindered and the flow of liquid and the rate of diffusion are much less than in the case of gases. The existence of

powerful forces of cohesion (forces between similar types of molecules e.g. H_2O) is responsible for the main properties of liquids.

The properties of liquid molecules are as under:

i. Additive properties:

Such properties depend upon the number and kind of atoms present in the molecule e.g. molecular weight.

ii. Constitutive properties:

Such properties depend upon the arrangement of atoms in the molecules and not their number e.g. optical activity.

iii. Colligative properties:

Such properties depend on the number of ions and molecules present but do not depend upon the structure of molecules. e.g. Osmotic pressure etc.

When a liquid is heated, its V.P. increases due to the decrease of intermolecular forces with rise in temperature. As a result more and more vapours escape in the air. A stage reaches at which the liquid begins to boil. So the **temperature at which the vapour pressure of the liquid equals to atmospheric pressure or some external pressure is called boiling point of that liquid.**

e.g. Boiling Point of water at 760mmHg = 100°C

Boiling Point of water at 23.7mmHg = 25°C

Effect of Pressure on boiling point of a Liquid:

There are two practical applications regarding the effect of pressure.

i. Effect of increase of Pressure:

Food can be cooked easily in pressure cookers, which is a closed container. The vapours are not allowed to escape out and, therefore, develop more pressure. This increases the B.P of water. Pressure cookers help us in cooking the food quickly even at high altitude e.g. B.P of water at 2026mm Hg is 130°C

ii. Effect of decrease of pressure:

The liquids which decompose at their B.P can be obtained in the pure form under reduced pressure by vacuum distillation e.g. Glycerine has a B.P of 290°C at 760mmHg but it decomposes at its B.P. Now in order to get it in the pure form, the V.P is decreased to 50mmHg by vacuum pump. The B.P decreases to 210°C at 50 mmHg, so it boils without decomposition. In this way the liquids can be purified.

Evaporation is the process in which liquid molecules escape from the surface and enter the gas phase. It can be explained in terms of the energy possessed by the molecules on the liquid's surface. Surface molecules whose kinetic energies are higher than

SCIENCE TITBITS

Sweat evaporation is a natural cooling system for the human body

average kinetic energies, overcome the intermolecular forces that bind them to the liquid and enter the gas phase. After their escape, the average kinetic energy of the remaining molecules decreases. Therefore temperature of the liquid decreases, thus evaporation is a cooling process.

The factors which can affect the rate of evaporation are as follow:

i. Surface Area

The rate of evaporation increases with increasing surface area. This is because large surface area allows more molecules to evaporate.

ii. Intermolecular Forces:

The escaping tendency of molecules depends upon attractive forces between the molecules. the liquids with strong intermolecular forces have less evaporation. Thus water has less evaporation rate than petrol. This is because water has stronger intermolecular forces (H-bonding) than petrol which has weak dispersion forces between the molecules. A liquid which can rapidly change into vapours is called **volatile** e.g. petrol is more volatile than water.

iii. Temperature

Evaporation takes place at all temperature. Rate of evaporation however is affected by the change in temperature. Increase in temperature increases the number of molecules having kinetic energy sufficient to overcome intermolecular forces and escape more readily from the surface of the liquid. Thus the rate of evaporation increases with increasing temperature. This is why clothes dry more readily in summer.

In open containers, evaporation continues until all of the liquid disappear. But when a liquid is placed into a closed container, amount of liquid decreases for a period of time and then does not change. In closed containers, the vapours cannot escape. Therefore, as the vapour concentration increases, some of the vapour molecules lose energy and return to the liquid state. This process is called condensation.

Evaporation involves molecules leaving the liquid and condensation occurs when a vapour changes back to a liquid. When the liquid is placed in a closed container, it begins to evaporate at a constant rate, very little condensation takes place. But as the concentration of the vapour increases above the liquid, the rate of condensation increases. After some time the rate of condensation equals the rate of evaporation. At this stage, the number of molecules entering the gas phase equals the number returning to the liquid phase, the system is said to be in a dynamic equilibrium. **"The pressure exerted by vapours in equilibrium with its liquid state is called the liquid's vapour pressure at the given temperature".**

Factors affecting Vapour Pressure

Vapour pressure is measured in the same units used for gas pressure. Vapour pressure is independent of the amount of liquid, so this is called an **intensive property** of the liquid. Two factors affect liquid's vapour pressure:

- Intermolecular forces
- Temperature

i. Intermolecular forces

The vapour pressure of a liquid depends upon the strength of intermolecular forces. Liquids having stronger intermolecular forces possess low vapour pressure and vice versa.

For example, water having hydrogen bonding possesses low vapour pressure. On the other hand ether, petrol etc have high vapour pressure due to weak dispersion forces.

ii. Temperature

As the temperature increases, the vapour pressure increases. This is because increase in temperature increases the average kinetic energies of the molecules which in turn decreases the intermolecular forces. For example, vapour pressure of water at 0 °C is 4.6 mm of Hg but at 100°C it is 760mm of Hg. The relationship of vapour pressure and temperature is shown by the graph (see Fig 5.3).

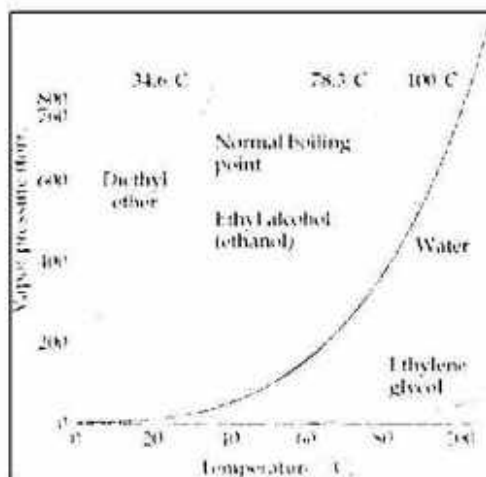


Fig 5.3: Effect of Temp on vapour pressure

Notice that the vapour pressure of diethyl ether (185mm Hg) at 0° C is much greater than that of ethanol (12mm Hg) or water (4.6mm Hg). Ether is non-polar in nature. Therefore, its high vapour pressure is due to its weak intermolecular forces (dispersion forces). Thus at the surface ether molecules require less energy to break free and change into vapour. Similarly, in ethanol intermolecular forces (H-bonding) are not as strong as those of water. Consequently vapour pressure of ethanol is greater than that of water at all temperatures.

It is observed that each of the three vapour pressure curves cross the line corresponding to one atmosphere at different temperatures. Therefore they boil at different temperatures. Ether boils at 35 °C, ethanol at 78 °C and water at 100 °C.

It is common observation that water can be poured very quickly from one container to another as compared to honey and glycerine. **The resistance of a liquid's to flow is called its viscosity.** The larger the viscosity, the more slowly the liquid flows. Viscosity measures, how easily molecules slide by one another. To understand viscosity, consider a liquid flowing in a tube is made up of a series of concentric circular layers. The resistance to flow is due to the internal friction between the layers of the molecules. The layers adjacent to the walls have the lowest velocity. Each layer exerts a drag on one another and thus causes resistance to flow.

Units:

SI units of viscosity is Pascal Second (Pa.s). Non-SI unit of viscosity is poise.

1 poise = $0.1 \text{ kg m}^{-1} \text{ s}^{-1}$ or $\text{g cm}^{-1} \text{ s}^{-1}$

1 Pa.s = $1 \text{ kgm}^{-1} \text{ s}^{-1} = 10 \text{ poise}$

**Factors Affecting Viscosity:**

Viscosity depends on the following factors:

- Molecular shape and size
- Intermolecular forces
- Temperature

i. Molecular shape and size

Molecular size and shape strongly influence viscosity. Liquids such as water, acetone, benzene and methanol, whose molecules are small and compact have low viscosity. Whereas liquids having large and irregular shaped molecules like honey, glycerine tends to get tangled up with each other. This inhibits the flow of molecules and leads to high viscosity.

DO YOU KNOW

In winter the viscosity of blood increases due to cold. The arteries and veins of human body contract and become hard and their diameter decrease. As a result the flow of blood and blood pressure is affected. On sitting before fire, the viscosity of blood decreases and its circulation increases. So the man becomes normal.

ii. Intermolecular forces

Stronger the intermolecular force among the molecules higher is the viscosity. Liquids whose molecules form hydrogen bonds are more viscous than other without hydrogen bonding. For example water is more viscous than methanol mainly due to extensive hydrogen bonding.

iii. Temperature

Molecules move faster as temperature increases. This is because; an increase in temperature decreases the intermolecular forces. This dependence is quite noticeable for highly viscous liquids such as honey and syrup. It is easier to pour these liquids when hot than when cold.

4. Surface Tension

Have you ever seen insects such as the water strider to walk on water? What allows it? Surface tension is the property of the surface of the liquids to act as if there is a membrane stretched across it. We can understand that the level of liquids exhibit surface tensions. All molecules below the surface of the liquid are surrounded in all directions by other molecules. Thus the force exhibited by such molecules is balanced in all directions whereas a molecule at a liquid surface has molecules beside it and beneath it but no one above it. This results in an unbalanced force pulling the surface molecules inward.

The molecules at the surface therefore, feel a net attraction inwards, which creates surface tension. **"The force in dynes acting at right angle on a unit length of surface of a liquid is called surface tension"**. For a molecule to come to the surface, it must overcome the attraction directed downward. This means work has to be done to pull it to surface. Therefore, increase in surface areas of a liquid requires an input energy. **Surface tension can also be defined as the amount of energy required to expand the surface of a liquid by a unit area.** Molecules at the surface of a liquid are less stable than those inside it, so a liquid is stable when the fewest molecules are at its surface. This occurs when the liquid has minimum

surface area. Spheres have less area per unit volume than any other. Therefore small drops of a liquid tend to be spherical.

Factors Affecting Surface Tension

Surface tension of a liquid depends upon the following factors.

i. Intermolecular forces

Surface tension of a liquid depends directly on the strength of intermolecular forces. Stronger the intermolecular forces among the molecules of liquid, greater is the surface tension and vice versa. For example the surface tension of water is higher than many liquids such as alcohols, ethers benzene etc. this is due to strong hydrogen bonding between water molecules.

ii. Temperature

Surface tension of a liquid decreases with the increase of temperature. This is because increased kinetic energy of the molecules decreases strength of intermolecular forces.

iii. Nature of Liquids

It is different for different liquids due to the presence of different types of intermolecular forces.

Units

SI unit of surface tension is joule per square meter, Jm^{-2} or Newton per meter, Nm^{-1} .

Why water does not expand like many substance? In ice hydrogen bonds hold water molecules in a rigid but open hexagonal structure. As ice melts, some of the hydrogen bonds are overcome, and water molecules move into the holes that were present in ice structure. As a result, the H_2O molecules are closer together in liquid water than in ice. When ice melts, there is a about 9% decrease in volume and a corresponding increase in density. So, water is most unusual in this regard, because the liquid state is less dense than the solid for most substances. If we continue to heat water just above the melting point, more hydrogen bonds are overcome. The molecules become still more closely packed and the density of liquid increases to a maximum density at 3.98°C . Below 3.98°C the density of water decreases with temperature, as we expect for a liquid. These density phenomena explain why a freshwater lake freezes from the top down in winter. When temperature falls below 4°C , the more dense water sinks to the bottom of the lake. The colder surface water freezes first. Since ice is less dense than water, the water that freezes remain at the top to cover the lake with a layer of ice. This layer of ice insulates the water underneath. Thus under this thick blanket of ice, fish and plants survive for months.

Hydrogen bonding in water contributes to its unique properties, which are as follows.

i. High surface tension

A stretched membrane is formed on the surface of water. The force on the surface acting downwards is due to strong hydrogen bond in water. Therefore a high surface tension is



observed. This has been proved by the following data. Which liquid has lowest surface tension.

Solvent	Surface tension ($\gamma \times 10^{-2}$) (Nm ⁻¹)
Water	7.275
Methanol	2.26
Ethanol	2.28
Benzene	2.888
Hexane	1.84
CCl ₄	2.70

ii. High specific heat:

Specific heat is the quantity of heat required to raise the temperature of 1g of the substance by 1°C (or by 1K). For example specific heat of water is 4.180J/g°C. It is much higher than those of metals. It takes almost ten times as much heat to raise the temperature of 1g of water 1°C as to raise the temperature of 1g of iron by 1°C. Conversely, much heat is given off by water even a small drop in temperature. The vast amounts of water on the surface of Earth thus acts as a giant heat reservoir to moderate daily temperature variations. That is why the climate near large bodies of water such as lakes, ponds, oceans etc, is more moderate than interior of the land.

iii. High heat of Vaporization:

Water has a high heat of vaporization due to extensive hydrogen bonding. A large amount of heat is required to evaporate a small amount of water. This is of enormous importance to us because large amounts of body heat can be dissipated by the evaporation of small amounts of water (perspiration) from the skin. This effect also accounts for the climate-modifying property of lakes and oceans.

iv. High boiling points

Water has a high B.P. due to strong H-bonding. It is practically observed that the B.P. of water is 100°C at one atmospheric pressure (760mm) at sea level, however, the organic solvents like benzene (B.P80°C), ether (35°C) etc. have lower B.P. due to poor interactions between the molecules.

5.4 ENERGETIC OF PHASE CHANGES

Physical and chemical changes are accompanied by energy change in the form of heat. A physical change in energy is the quantitative measurement of the strength of intermolecular forces. Energy change at constant pressure is known as enthalpy change denoted by ΔH . It is expressed in kJ mole⁻¹. When a substance undergoes a phase change (change of state), its temperature remains constant, even though heat is being added.

5.4.1 Molar Heat of Fusion, Molar Heat of Vaporization and Molar Heat of Sublimation

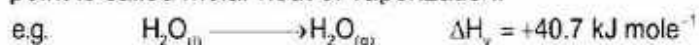
Molar heat of fusion (ΔH_f) is the amount of heat required to convert one mole of a solid into its liquid state at its melting point is called molar heat of fusion (ΔH_f)

e.g. Molar heat of fusion for ice is $+6.02 \text{ kJ mole}^{-1}$



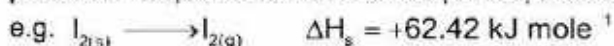
Molar heat of vaporization (ΔH_v)

The amount of heat required to convert one mole of a liquid into its vapours at its boiling point is called molar heat of vaporization.



Molar heat of Sublimation (ΔH_s)

The amount of heat absorbed when one mole of a solid sublimates to give vapour at a particular temperature at one atmospheric pressure is called molar heat of sublimation.



5.4.2 Energy Changes and Intermolecular Forces

As a result of melting of a solid, a small change in intermolecular distance and potential energy takes place in atoms, molecules or ions. On the other hand on evaporation of a liquid atoms, molecules or ions undergo large changes in their intermolecular distance and potential energy. Therefore, heat of vaporisation is much greater than that heat of fusion.

Particular examples:

- ΔH_v (heat of vapourization) for H_2O ($40.6 \text{ kJ mole}^{-1}$ at 373.15K , for NH_3 ($23.35 \text{ kJ mole}^{-1}$ at 239K) and CO_2 ($25.23 \text{ kJ mole}^{-1}$ at 194.5K) are high due to their polar nature and strong intermolecular forces ΔH_f (Heat of fusion) will be as under:

$$\text{H}_2\text{O} = 6.02 \text{ kJ mole}^{-1} \text{ at } 273.15\text{K}$$

$$\text{NH}_3 = 6.652 \text{ kJ mole}^{-1} \text{ at } 195.4\text{K}$$

$$\text{CO}_2 = 8.33 \text{ kJ mole}^{-1} \text{ at } 217.0\text{K}$$

- I_2 , a volatile solid has the highest value of Heat of sublimation i.e $62.42 \text{ kJ mole}^{-1}$ at 458.4K . The values for other halogens are

$$\Delta H_v \text{ for } \text{Br}_2 = 29.4 \text{ kJ mole}^{-1} \text{ at } 332.4\text{K}$$

$$\text{for } \text{Cl}_2 = 20.21 \text{ kJ mole}^{-1} \text{ at } 239.1\text{K}$$

$$\text{for } \text{F}_2 = 3.16 \text{ kJ mole}^{-1} \text{ at } 85.0\text{K}$$

This shows that ΔH_v (heat of vapourization) of I_2 is the highest because of strong intermolecular forces than the other halogens.



Dynamic equilibrium is a reversible process where the two opposite changes occurring simultaneously at equal rates. For example solid to liquid or liquid to gas and vice versa. The system moves towards the condition of dynamic equilibrium.

example At 0 °C, ice exists in dynamic equilibrium with liquid water.



In 1888 an Austrian Botanist, Frederick Reintizer discovered that when crystals of cholesteryl benzoate are heated, it forms a milky liquid at 145°C. On further heating, the milky liquid suddenly becomes clear. When the clear liquid is cooled, the reverse process occurs. The milky or turbid liquid is called liquid crystal. The liquid crystal state exists between two temperature i.e. melting temperature and clear temperature. It is a form of matter intermediate in characteristics between a liquid and solid crystal. They have properties of liquids and show viscosity, surface tension etc.

Definition

- (i) The substance which can flow like a liquid and also have some of the properties of liquids within a certain temperature range are called liquid crystals.
- (ii) The intermediate phase lying between the solid phase and the normal liquid phase is called liquid crystal.

Uses in daily life

- i. Liquid crystals are used as temperature sensors. This is because the liquid crystals change their colour with change in temperature.
- ii. They are used to monitor temperature changes where conventional methods are not feasible, e.g. they are used in thermometer for measuring skin temperature of infants.
- iii. Some of the modern room thermometers contain liquid crystals with a suitable temperature range. As temperature changes, the liquid crystal show up the figure in different colours.
- iv. They are used to find the point of potential failure in micro-electronic circuits.
- v. They are used to locate the veins, arteries and tumours, e.g. when a layer of liquid crystal is painted on the surface of the breast, a tumour shows up as a hot area which is coloured blue. Thus this technique helps in early diagnosis of breast tumours.
- vi. Liquid crystals are used in the display of numbers and letters of electrical devices such as digital watches, calculators and computers etc.
- vii. Liquid crystals are used in LCD screens of oscillographs and TV.



Science Titbits

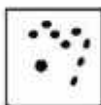
The mucous secreted by slugs and snails behaves like liquid crystals. Its rod-shaped molecular arrangements align in varying degrees to control the viscosity of the mucous to adapt to different ground conditions.



- A liquid crystal is a state of matter which is in between pure liquid (transparent) and crystalline solid.
i.e. crystalline solid $\rightleftharpoons$ liquid crystals $\rightleftharpoons$ pure liquid
- A liquid crystal resembles the crystalline solid in certain respects, e.g. optical properties. However pure liquids remain as such.
- A crystalline solid may be isotropic (A substance showing same properties in all directions) and an anisotropic (A substance showing different properties in different direction) but liquid crystals are always isotropic. Pure liquids remain as such.
- Liquid crystal is intermediate in between pure liquid and crystalline phase.

References for additional information

- Holderness & Lambert, A New Certificate Chemistry.
- John Olmsted III and Gregory M. Williams, Chemistry, The Molecular Science.
- Osei Yaw Ababio, New School Chemistry.
- George M. Bodner and Harry L. Pardue, Chemistry, an experimental Science.



1 Choose the correct answer (MCQs).

- Van Der Waal's forces are effective;
 - (a) At long distance
 - (b) Both at long as well as short distance
 - (c) Only at short distance
 - (d) Independent of distance
- Which one of the following forces are also called London forces?
 - (a) Ion-dipole forces
 - (b) Dipole-induced dipole forces
 - (c) Dipole-dipole forces
 - (d) Dispersion forces
- Which of the following two halogens are gases at room temperature?
 - (a) Fluorine and Iodine
 - (b) Chlorine and Bromine
 - (c) Fluorine and Chlorine
 - (d) Iodine and Bromine
- The intermolecular forces are of;
 - (a) Two types
 - (b) Three types
 - (c) Four types
 - (d) Five types
- Thermostat is an instrument which;
 - (a) Increases the temperature
 - (b) Decreases the temperature
 - (c) Maintains the temperature
 - (d) Fluctuate the temperature



- vi. The scientist who discussed the phenomenon of viscosity are;
(a) Poiseuille (b) Newton
(c) Fritz (d) Vander Wall
- vii. The distillation under reduced pressure is called;
(a) Fractional distillation (b) Vacuum distillation
(c) Steam distillation (d) Pressure distillation
- viii. The unit of surface tension is;
(a) Newton per metre (b) Newton per metre square
(c) 760mmHg (d) Newton square per metre
- ix. The intermediate phase lying between the solid phase and the normal liquid phase is called;
(a) Crystalline solid (b) liquid crystals
(c) Mesogens (d) Crystal lattice
- x. In which of the following are the particles the most disordered?
(a) Water at 100 °C (b) Steam at 100 °C
(c) Impure water at 102 °C (d) Water at 10 °C
- xi. Which of these statement best supports the idea that matter is made up of particles?
(a) Liquids always fill the space available to them
(b) Liquids are easily compressible
(c) 1 cm³ of water produces nearly 1700 cm³ of steam
(d) If a bottle of perfume is opened, the smell spread quickly
- xii. Which of these processes involve a weakening of the attraction between particles?
(a) Condensation (b) Freezing
(c) Crystallization (d) Evaporation
- xiii. A liquid is thought to be pure ethanoic acid (acetic acid), which of the following is the best way to test its purity?
(a) Measure its B.P
(b) React it with ethanol
(c) Burn it completely in oxygen
(d) Dehydrate it with concentrated H₂SO₄

2: Write brief answer to the following.

- i. Give the general properties of liquids as to
(a) Diffusion (b) Compression
- ii. What are the types of intermolecular forces, give examples?
- iii. What is hydrogen bonding, give particular examples?
- iv. What are the applications of H-bonding?
- v. What are the different types of physical properties of liquids?



- vi. Define vapour pressure. What are the factors affecting the V.P?
 - vii. What is
 - (a) Viscosity.
 - (b) Surface tension.
 - viii. Define molar heat of fusion and molar heat of vaporization.
 - ix. How will you differentiate liquid crystals from pure liquids?
 - x. Why distillation under reduced pressure is often used in the purification of chemicals?
- 3 (a) Give the simple properties of liquids with special reference to the following:
- Diffusion
 - Compression
 - Expansion
 - Inter molecular forces
 - Kinetic energy
- (b) Explain on the basis of kinetic molecular theory. Why the boiling point of a liquid remains constant although heat is continuously supplied to the liquid?
- 4 (a) Define and explain evaporation.
- (b) What are the factors affecting evaporation?
- (c) Different liquids have different rates of evaporation. Explain with reference to ether and alcohol?
- 5 (a) Define and explain vapour pressure. How equilibrium is established between evaporation and condensation?
- (b) What are the factors affecting vapour pressure of a liquid?
- (c) Kinetically how will you explain the effect of temperature on vapour pressure?
- 6 (a) Define and explain boiling point of a liquid?
- (b) How will you explain the effect of pressure on the boiling point of a liquid?
- (c) Practically how will you explain the
- (i) Effect of increase of pressure on boiling point.
 - (ii) Effect of decrease of pressure on boiling point.
- 7 (a) Define and explain the term viscosity of a liquid? How does the resistance to the layers causes viscosity?
- (b) What are the factors affecting the viscosity of a liquid?
- (c) Use the concept of hydrogen bonding to explain the following properties of water?
- (i) High surface tension
 - (ii) High heat of vaporization
 - (iii) High boiling point



- 8
 - (a) Define and explain the phenomenon of surface tension?
 - (b) What are the factors affecting surface tension?
 - (c) Define dynamic equilibrium between two physical states?
 - (d) Define?
 - (i) Molar heat of fusion
 - (ii) Molar heat of vapourization
- 9
 - (a) Define a liquid crystal?
 - (b) What are the uses of liquid crystals in daily life?
 - (c) How will you differentiate liquid crystals from pure liquids and crystalline solids?
- 10 What are the energetics of phase changes?
- 11
 - (a) Define and explain the boiling point of a liquid?
 - (b) How will you explain the two practical applications regarding the effect of pressure on the boiling point of a liquid?
- 12 How can you interpret the anomalous behaviour of water?



SOLIDS



This is a 10 days unit

After completing this lesson, you will be able to:

- Define lattice energy.
- Describe simple properties of solids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on kinetic molecular theory.
- Differentiate between amorphous and crystalline solids.
- Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature.
- Use oxygen and sulphur to define allotropes.
- Name three factors that affect the shape of an ionic crystal.
- Explain the low density and high heat of fusion of ice.
- Define and explain molecular and metallic solids.
- Explain the significance of the unit cell to the shape of the crystal using NaCl as an example.
- Name three types of packing arrangements and draw or construct models of them.
- Differentiate between ionic, covalent, molecular and metallic crystalline solids.



Reading

INTRODUCTION

The characteristics of the solid state are that the substance has definite shape. Due to the strongest inter-molecular forces existing between the molecules, it is little affected by changes in temperature and pressure. Glasses and amorphous materials are the exceptions where there is no orderly arrangement of atoms. Such solids are called super-cooled liquids. Other solids have complete regularity of their atomic and molecular structures. Such solids are called crystals.

It is observed that some kind of forces exists between the ions, atoms or molecules which keep them together in a crystalline solid. This gives a definite shape, rigidity and mechanical strength to the solids. Such forces are called inter-ionic inter-molecular and inter-atomic forces. These forces are of different types in different solids. As a result the solids have different physical properties.

6.1 KINETIC MOLECULAR INTERPRETATION OF SOLIDS

Kinetically the crystalline solids can be interpreted as follows:

i. Attractive Forces:

The attractive forces among the molecules are maximum due to closest packing of the molecules.

ii. Rigidity:

The molecules in solids are closely packed. Therefore their movement is restricted (limited). As a result they are rigid in nature. The molecules cannot move due to maximum attractive forces between them. However, molecules vibrate about their mean position.

- iii. **High density:** $d = \frac{m}{V}$
 The molecules of a crystalline solid are closely packed. As a result, molecules of solid occupy minimum volume. As density is inversely proportional to volume, therefore high density will be observed due to the minimum volume existing between the molecules.
- iv. **Collision:**
 As there is no translational movement of particles in a solid, therefore, there are no collisions among the molecules.
- v. **Kinetic Energy:**
 There is negligible translational and rotational kinetic energy in solid molecules. However they can vibrate about their mean positions. So molecules of solid possess only vibrational K.E.
- vi. **Geometric Shape:**
 The crystalline solids have definite distinctive geometrical shape. It is due to the definite and orderly arrangement of atoms, ions or molecules in three dimensional shape.

6.1 Properties of Solids

Some simple properties of solids are diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on Kinetic Molecular Theory.

Explanation of Properties

i. Diffusion:

The diffusion depends upon velocity of molecules. As the movement of the molecules is very slow, therefore, the diffusion will be minimum. Had there been diffusion in solids? The centuries old buildings would have collapsed in no time.

ii. Compression (Effect of Pressure):

There is practically no effect of pressure on solids as the molecules are very closely packed together.

The effect of pressure on solids is expressed in terms of compressibility (β). This is defined as, "The decrease in volume per unit volume when the pressure is increased by one atmosphere." $\beta = \frac{\Delta V}{V}, \text{atm}$

iii. Expansion: (Temperature)

The solids expand when heated i.e. their volume increases. This is because the increase of temperature decreases the intermolecular attractive forces. As a result, the volume increases.

The co-efficient of expansion (α) is defined as "the increase in volume per unit volume when the temperature is increased by 1°C ." When a solid is heated, its geometric shape

$$\alpha = \frac{\Delta V}{V}, 1^\circ\text{C}$$

The student should be also guided to recall the information.

changes until at a certain temperature, it changes into the liquid form. The temperature at which a solid, changes into the liquid form is called Melting Point of the solid."

iv. Motion of Molecules:

There is no translational and rotational motion due to presence of strong intermolecular forces in the crystalline solid, as the molecules are already closely packed together. However the molecules can vibrate about their mean position.

v. Intermolecular Forces:

In solids, the intermolecular forces are maximum in between the particles. These are held together in fixed positions by strong attractive force. They can vibrate only about their fixed positions.

vi. Kinetic Energy Based Upon Kinetic Molecular Theory:

According to the Kinetic Molecular Theory, the attractive forces between the solid particles are maximum. This is due to minimum distance between them and, therefore, molecules do not possess translation and vibrational kinetic energies. However, they can vibrate about their mean positions. So they possess vibrational kinetic energy.

6.2 TYPES OF SOLIDS:

There are two types of solids:

Do You Know

Metallic glasses are new amorphous materials composed of metallic alloys atomic with disordered atomic structure.

i. Amorphous Solids:

The solids which have no definite geometric shape are called amorphous solids e.g. glass, rubber, dust etc.

ii. Crystalline Solids:

The solid, which have a definite regular and three-dimensional geometric shape are called crystalline solids. Some crystalline solids have certain molecules of water of crystallization e.g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

6.2.1 Differences between Amorphous and Crystalline Solids

- 1) In the crystalline state, the crystals possess definite geometrical structure e.g. NaCl is cubic in nature. In the amorphous state the solids do not have definite geometrical structure e.g. glass.
- 2) There is a complete regularity of arrangement of atoms, ions or molecules in a crystalline solid whereas the atoms, ions or molecules are not arranged in a regular manner in amorphous solids.
- 3) The crystalline substance has a sharp Melting Point while the amorphous solid do not have sharp Melting Point and gradually soften on heating. They may be called as super-cooled liquids e.g. glass, plastic etc.
- 4) In a crystalline substance, water molecules are a part of crystal e.g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ etc while the amorphous substances have no such water of crystallization.



The student should be guided to remember information.

6. Solids

- 5) In some cases, the colour of a crystalline substance is due to water of crystallization e.g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue. The colour of crystals fades away in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ when it is heated.
- 6) The amorphous solid is a solid which softens on heating ultimately they become mobile over a wide range of temperatures while the crystalline substances have no such property.

Crystal lattice $\rightarrow$ X-Ray of Crystal

6.3 PROPERTIES OF CRYSTALLINE SOLIDS

Some important properties of crystalline solids are described here:

Geometrical Shape:

Almost all the crystalline solids have a definite, distinctive geometrical shape because the molecules have fixed positions. Therefore they cannot move appreciably. Moreover the solids have orderly arrangement of atoms, ions or molecules in three dimensional space e.g. NaCl is cubic in nature.

Melting Point:

Pure crystalline solids have sharp melting point. When a solid is heated, the atoms, ions or molecules present in a solid start vibrating at higher frequency and transfer their kinetic energy throughout the solid. At the melting point, their vibrational energies become so much that they leave their fixed positions simultaneously and become a liquid.

(Break down)

Cleavage Planes:

A crystalline solid contains atoms, ions or molecules closely packed to each other. When some external pressure is applied to it, it changes into small crystals of the same size and shape as that of the original one.

The breaking up of larger crystals into smaller one with identical size and shape is called cleavage. The plane which contains the direction of cleavage is called cleavage plane.

- e.g. (i) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystal can be cleaved easily provided cleavage is parallel to the surfaces.
- (ii) The cleavage of NaNO_3 and $(\text{CH}_3\text{COO})_2\text{Ca}$ is easy. It is parallel to the surface.
- (iii) Mica can be cut easily parallel to the layers.

Habit of a Crystal:

Almost all the solids have particular no. of faces under identical conditions e.g. NaCl is cubic with six faces. But if an impurity is present, the solid material changes its structure because new faces are produced in addition to the original one.

The shape of a crystal in which it usually grows is called habit of a crystal. For example cubic crystals of sodium chloride are obtained from its aqueous solution. If the conditions are changed, the shape of crystal also changes. If 10% urea is present in aqueous solution of sodium chloride, octahedral crystals of sodium chloride are obtained.

v. **Crystal Growth:**

The crystal growth takes place when the heated solution of a substance is allowed to cool in a slow manner. The outer appearance or shape of the crystals depends on how it is prepared and under what condition e.g. a crystal with cubic structure may develop into a cube, a flat plate or a long needle like structure, under different conditions. The size of a crystal is controlled by its rate of growth. A slowly growing crystal has large size.

vi. **Anisotropy:**

A crystalline substance is built up of small units all having the same geometrical form. But although a crystal is homogeneous, it possesses different properties in different directions. It is because crystal has different arrangements in different directions e.g. graphite exists in the form of layers, so it is conductor in one direction, parallel to layers but insulator across the layers.

A substance which shows different intensity of properties in different directions is called anisotropic and this property is called anisotropy. e.g. Refractive index, co-efficient of thermal expansion, electrical and thermal conductivities give different intensity of properties in different directions. e.g. Mica can be cut parallel to the layers but difficult to cut in some other plane.

vii. **Symmetry:**

There are certain crystalline substances which after rotation to certain angles give similar edges, corners or faces at definite distances in definite directions. The rotational operation which brings the crystals into its original appearance is called symmetry of element; e.g. if a regular cube is rotated about its axis at an angle of 90° , the identical face is obtained. On rotating to 180° , a second identical face and at 360° , four identical faces are observed. An axis containing four identical faces is called four-fold axis of rotation. The process through which the crystal was brought back to its identical position is called symmetry operation.

An imaginary plane passing through a crystal that divides a crystal into two identical halves is called plane of symmetry. The symmetry elements that occur in a crystal are plane of symmetry, centre of symmetry, axis of symmetry and angle of symmetry.

iii. **Isomorphism:**

There are certain substances which are similar in shape. Different crystalline substances having the same crystalline shapes are called isomorphs, and this phenomenon is called isomorphism; due to having same ratio of atoms.

e.g. (i) ZnSO_4 and NiSO_4 are isomorphism because both have the same crystalline shape i.e. orthorhombic. isomorphs have same atomic ratio.

(ii) Ag_2SO_4 and Na_2SO_4 are hexagonal. (Atomic ratio = 2:1:4)

(iii) CaCO_3 and NaNO_3 are Rhombohedral. (Atomic ratio = 1:1:3)

The student should be guided to recognize the information

xiv. Polymorphism:

The substance existing in more than one crystalline form is called polymorphous substance and the phenomena as polymorphism.

- e.g.
1. NaCl is found in cubic and octahedral forms.
 2. CaCO_3 is trigonal when present as calcite and orthorhombic when present as aragonite.
 3. HgI_2 is orthorhombic (yellow form) and tetragonal in red form.

xx. Allotropy (allotrope – Greek-allos (other), tropia (turning): (forms)

An element may exist in different crystalline forms. These forms are called Allotropes and this phenomenon is called allotropy.

- e.g.
- (i) C (as diamond) _____ in cubic form.
 - (ii) C (as graphite) _____ in hexagonal form.

xxi. Transition Temperature:

The temperature at which more than one forms of a given substance can exist in equilibrium is called transition temperature. Above and below this temperature only one polymorph or allotrope can exist.

No	Substance	Crystalline form	Transition temperature
1	Tin (grey) Tin (white)	Orthorhombic Tetragonal	18 °C
2	Sulphur	Monoclinic Ortho rhombic	95.6 °C
3	KNO_3	Orthorhombic Rhombohedral	128.5 °C

Allotropes of Oxygen

Dioxygen (O_2) and Trioxygen (O_3 or Ozone) are considered to be the two forms of oxygen obtained by the absorption of certain amount of heat from atmosphere.

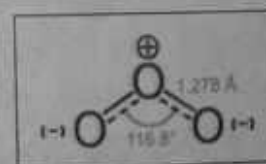
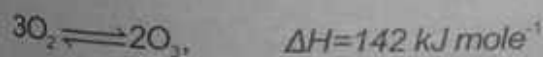


Figure 6.4: Shape of an ozone molecule

The student should be guided to list given information.

Explanation to form Allotropes

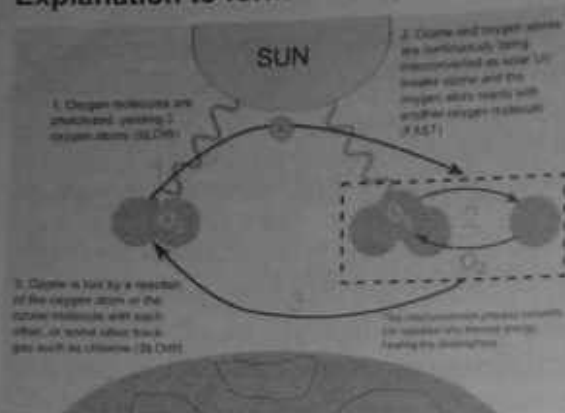


Figure 6.5 How ozone protects earth

Certain amount of heat is absorbed by dioxygen to form trioxxygen i.e. ozone, the ultraviolet (U.V) light in the form of energy brings about photo-chemical reactions. These reactions can convert oxygen (O_2) to ozone (O_3). Since the conversion is spontaneous and one directional, therefore, it is called monotropic (moving in one direction). It has been found that the maximum concentration of ozone is (about 10 ppm) (parts per million), occurs 24-30 Km from the surface of the earth. Thus oxygen has two allotropic forms which are irreversible.

Structures

Oxygen molecule $O = O$ has a sigma (σ) bond and a Pi-bond (π) between the two atoms. In ozone molecule, there is an angle of 117° between the bonds as indicated.

The ozone layer in the stratosphere (one of the layer of atmosphere) is shown below.

The allotropes of oxygen are of two types:

- (i) Oxygen (O_2) (ii) Ozone (O_3)

Ozone has a characteristic smell, in concentration above 1000 ppm, it causes health hazards.

Allotropes of Sulphur

Sulphur exists in four allotropic forms which are:

- i. **Rhombic Sulphur (α -Sulphur):** It is bright yellow in colour and stable below $96^\circ C$. It is crystalline in nature and made up of S_8 molecules.
- ii. **Monoclinic Sulphur (β -Sulphur):** It is a crystalline solid and stable between $96^\circ C$ and $119^\circ C$. It is converted to Rhombic Sulphur at room temperature.

$$2H_2S_{(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} + 2S_{(s)} \text{ (amorphous solid)}$$
- iii. **Plastic Sulphur (γ -Sulphur):** It is a super cooled form of sulphur. If yellow sulphur is heated to boiling and poured into liquid water, it will roll up and produce yellow ribbons resembling plastic like material. It is not considered to be a true allotrope of sulphur because it is soft and elastic in nature and insoluble in H_2S .
- iv. **Amorphous Sulphur:** It has irregular crystalline shape which may be called as Amorphous. It is not found in the free state. It may be prepared by passing H_2S gas through water for a long time. The saturated solution of H_2S so obtained is exposed to air. Amorphous sulphur so produced has almost white colour.

6.4 CRYSTAL LATTICE:

153

The regular arrangement of the particles of a crystalline solid at the microscopic level produces characteristic shapes of crystals. The position of the particles in a crystalline solid is represented by a Lattice. An array of points representing the arrangement of particles (atoms, ions or molecules) in three dimensional spaces is called crystal lattice.

The external shape of a crystal depends upon the conditions of crystallisation. It may be different in one form or the other e.g. NaCl is cubic at ordinary conditions but octahedral in the presence of urea as impurity. But the internal structure is the same with basic structural unit. This unit describes the pattern by which the particles are arranged in a crystal. Primarily a crystal depends upon,

- Shape of the unit cell.
- Contents of the unit cell.

The atoms, molecules or ions in a crystal are repeated in a systematic manner. The **smallest unit of volume of a crystal, which shows all the properties of its pattern, is called a unit cell.** This is a basic structural unit of a crystal. The systematic arrangement of atoms in a crystal is called lattice. It represents the structure of any substance.

A lattice is of three types:

- Three dimensional lattice.
- Two dimensional lattice.
- One dimensional lattice.

6.4.1 Unit Cell and Shape of NaCl

We can explain significance of unit cell to the shape of crystal using NaCl as an example.

The unit cell is primarily concerned with the shape of the crystalline substance. Keeping in view the shape of the crystal, its structure can be identified. Let us take the example of NaCl.

- Location of ions:** In NaCl, each Na^+ ion is surrounded by 6 Cl^- ions and vice versa. The size of Cl^- ion is bigger than Na^+ ion because Cl^- ion has 18 electrons and Na^+ ion has 10 electrons.
- Co-ordinate Number:** The number of negative ions which contact a unit positive ion is called its co-ordinate number. In NaCl each Na^+ ion contacts with 6 Cl^- ions at the corner of a regular octahedron. So the co-ordination number of Na^+ ion is 6. Similarly co-ordination number of Cl^- ion is also 6. The distance between all Na^+ ions and Cl^- ion is the same.
- No. of NaCl in Each Unit Cell:** In NaCl there are 8 Cl^- ions at each corner of the cube. Each Cl^- ion is shared among eight unit cells. Each face shares with two unit cells. So the number of Cl^- ion in each unit cell can be calculated.

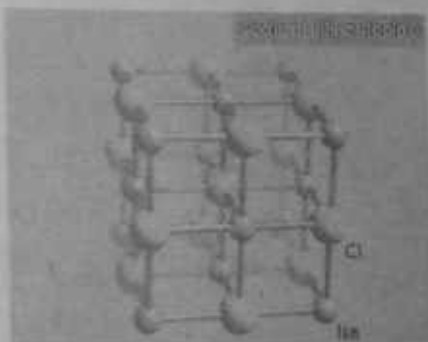


Figure 6.6: Structure of NaCl Crystal

(a) Calculation of Cl^- ions:

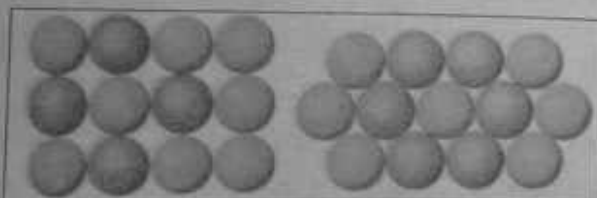
(i) No of unit cells = 8.

No of Cl^- ions at each corner of cube = 8Number of Cl^- ions in one unit cell at the corner = $\frac{8}{8} = 1$ (ii) Total number of Cl^- ions at the corner of a regular octahedron = 6

No of unit cells containing each face = 2

No of Cl^- ion in each unit cell at face centers = $\frac{6}{2} = 3$ Total number of Cl^- ion in each unit cell = $1 + 3 = 4 \text{ Cl}^-$ **(b) Calculation of Na^+ ions:** Na^+ ions are present at the edges.

No of edges present in the cube = 12

Number of unit cells of Na^+ ions = 4No of Na^+ ion present in each edge = $\frac{12}{4} = 3 \text{ Na}^+$ Na^+ ion present in the centre = 1 Na^+ Total number of Na^+ ions = $3 + 1 = 4 \text{ Na}^+$ ionsSo each unit cell consists of 4 Na^+ ions and 4 Cl^- ions.Hence $4 \text{ Na}^+ + 4 \text{ Cl}^- = 4 \text{ NaCl}$ can be written.**6.4.2 Types of Packing Arrangements**

(a) An open packing

(b) Close packing

Fig. 6.7: Packing spheres in two dimensions.

The structure of metals can be explained when the atoms are packed together. The atoms in metals are considered as spheres of identical size. The closest packing is the most efficient arrangement of spheres of identical size and to fill available spaces. In which each sphere touches six neighbouring spheres (in green) as shown in (fig 6.7).

(b) Close Packing

This layer is shown in figure 6.8 as the bottom layer (layer A). When we place spheres in the second layer (layer B) each added sphere will rest in the hollow above a void or hole in the bottom layer. The spheres of the second layer will produce two types of voids. (i) a tetrahedral hole which falls above a sphere in the bottom layer. (ii) an octahedral hole, it falls above a void in the bottom layer.

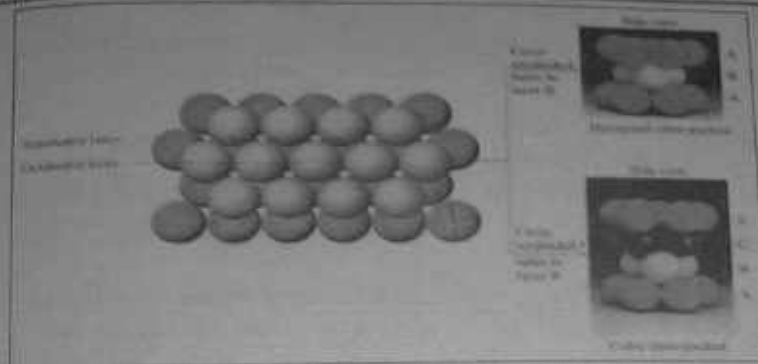


Fig. 6.8: Close-packing of spheres in three dimension

In adding a third layer of spheres (layer C), there are two possibilities.

- If tetrahedral holes are covered, the third layer is identical to the bottom layer. This arrangement is called hexagonal close-packing (hcp) arrangement. This pattern of arrangement is usually written as ABAB or 1212.
- In contrast, if we cover the octahedral holes, the third layer is not identical with the bottom layer. This is called the cubic close packing (ccp) arrangement. It is usually written as ABCABC or 123123.

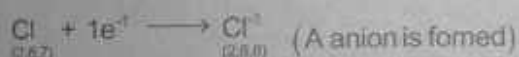
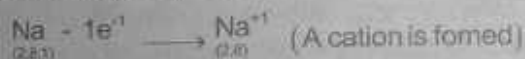
5.1 The Factors that Affect the Shape of an Ionic Solid

There are three factors which affect the shape of an ionic crystal.

Electrostatic Forces of Attractions:

The ionic solids are composed of cations and anions. They are held together through strong electrostatic forces of attraction forming a well defined geometric shape e.g. formation of NaCl.

Sodium loses one electron to be converted to Na^{+1} ions.



These ions combine together due to strong electrostatic force.



It is an exothermic reaction. To form a crystal lattice of NaCl, each Na^{+1} ion is surrounded by 6 Cl^{-1} ions and each Cl^{-1} ion is surrounded by 6 Na^{+1} ions. As a result a cubic structure of ionic solid of NaCl is formed.

The student may be guided to distinguish between different facts and figures.

2. Radius Ratio:

The structure and shape of an ionic solid depends upon the radius ratio of cations and anions e.g. NaCl and CsF have the different geometry because the radius ratio is different in both the cases.

$$\text{Radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion}}$$

The structure and Limiting radius ratio of certain crystalline substances are given below:

No	Shape of ionic solid	Limiting radius ratio r^{+}/r^{-}
1	Body centred cubic	0.732 and above
2	Octahedral	0.414 to 0.732
3	Tetrahedral	0.22 to 0.414
4	Triangular	0.15 to 0.22

Thus knowledge of radius ratio consisting of cations and anions can give a good idea of the shape of crystal. And ionic compound with radius ratio greater than 0.732 will have cubic structure e.g. NaCl.

Body centred

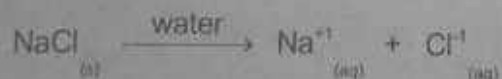
The radius ratio of an ionic compound with octahedral structure should be in between 0.414 and 0.732. Similarly a tetrahedral structure is formed if the radius ratio is in between 0.22 to 0.414.

The Radius Ratio of the following ionic crystals are:

1. NaCl = 0.522 – Octahedral arrangement or cubic structure.
2. CsCl = 0.93 – Body centred cubic arrangement.
3. ZnS = 0.40 – Tetrahedral arrangement.

3. Poor Conductivity:

The ionic crystals do not conduct electricity in the solid state. The shape of the crystals remains as such. However when a solvent (H_2O) is added to the ionic solid e.g. NaCl, the crystal lattice is broken and the ionic solid changes into cation and anion. This is because the crystal lattice is broken due to high dielectric constant of water. In other words the shape of the crystal is ruptured.



Thus the ions are solvated.

6.5.2 LATTICE ENERGY:

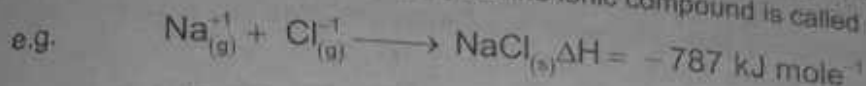
It may be defined on the basis of chemical reactions which may be exothermic or endothermic. The lattice energy can be defined in two ways.

The student may be guided to interpret concepts.

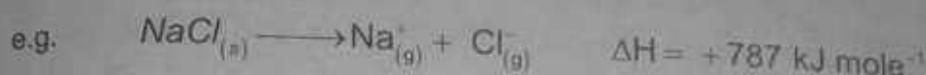
6. Solids

157

- The amount of heat or energy released when gaseous ions of opposite charges combine to give one mole of a crystalline ionic compound is called lattice energy.

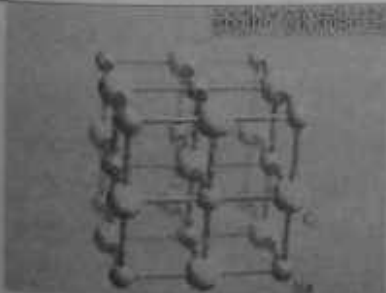
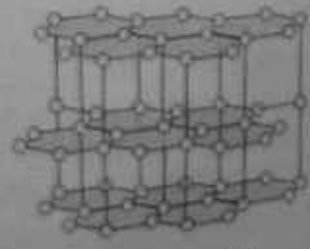


- The amount of energy required to break one mole crystal lattice into its gaseous ions is called lattice energy.



- The lattice energy of the ions depends upon their size and charge of the ions. Lattice energy decreases with the increase in the size of the ions. (whether cations or anions), the packing of oppositely charged ions become less and less tight. Lattice energy increases with increasing ionic charge.

5.3 Comparison of Ionic and Covalent Crystals

Difference Between	
Ionic Crystals (Solid)	Covalent Crystals
An ionic crystal is formed due to the transference of electrons to the other e.g. NaCl formation. The cations and anions formed are held together through strong electrostatic forces of attractions.	The crystalline solids in which atoms of similar or dissimilar elements are held together in a network of single bond are known as covalent crystals e.g. diamond etc.
Formation of NaCl $\text{Na}_{(2,8,1)} - e^{-1} \longrightarrow \text{Na}_{(2,8)}^{+1} \text{ (cation)}$ $\text{Cl}_{(2,8,7)} + e^{-1} \longrightarrow \text{Cl}_{(2,8,8)}^{-1} \text{ (anion)}$ $\text{Na}^{+1} + \text{Cl}^{-1} \longrightarrow \text{NaCl}$	Covalent crystals are of two types: (i) When covalent bonds give giant molecules e.g. diamond, SiC (Silicon carbide) (ii) When atoms join together by sharing of electrons. As a result separate layers are formed e.g. graphite.
 Sodium Chloride crystal	 Graphite crystal

3. They are non-conductors of electricity in the solid state. However they conduct electricity in the molten or solution form.	3. They are bad conductors of electricity with the exception of graphite.
4. They have definite geometric shape.	4. They have definite shape and oriented in three directions with a network structure.
5. They are non-directional in nature.	5. They have open structures due to the valences of atoms directed in definite directions.
6. They do not exist in the form of molecules due to their ionic nature.	6. They may be called as molecules due to their covalent nature. e.g. S_8 , P_4 , ice.

6.5.4 Low Density and high Heat of Fusion of Ice

i. Low density of ice

When the temperature is decreased the molecules come close to each other. As a result the intermolecular attractive forces increase. However some empty spaces are developed in the ice. As a result about 9% more space than liquid water is produced. As $d = \frac{m}{v}$, that is density is, inversely proportional to volume, the increase in volume decreases the density. That is why ice floats over water.

Application of Low Density in Real Life

In cold countries when temperature is decreased to 0°C , water in ponds and lakes freezes. The ice formed stays on the top. This layer of ice acts as insulator for further heat loss. A thick layer of ice is formed at the top. Fish and plants can survive in the water for months under the thick blanket of ice.

Keeping in view the above discussion, we are forced to believe that the pattern of life for plants and animals would have been totally different in the absence of Hydrogen bonding in water.

ii. High Heat of Fusion of Ice

The quantity of heat required to convert one mole of a solid into liquid is called molar heat of fusion.

e.g. Ice $\longrightarrow$ liquid water $\Delta H_f = 6.02 \text{ kJ mole}^{-1}$

Applications in Real Life

Ice absorbs 333 joules of energy for every gram of ice to melt. It means, if 33.3 k. Joules of energy from the surrounding is absorbed by each of the drink, the temperature of the drink without ice would rise from 0°C to 20°C . The drink containing the ice would remain at 0°C but 100 grams of ice would melt.

6.5.5 Molecular and Metallic Solids

Molecular Solids:

1. **Definition:** The solid substances in which the particles forming the solids are polar or non-polar molecules are called molecular crystals.
e.g. In solidified gases, these are non-polar atoms. Two types of intermolecular forces hold them together.

1. Dipole-Dipole interactions.
2. Van der Waal's forces.

Examples:

1. Crystals with polar molecules e.g. ice, sugar.
2. Crystals with non-polar molecules e.g. I_2 , S_8 , P_4 , CO_2 etc.

Properties:

1. X-ray analysis indicates the regular arrangement of atoms. Thus we get the exact positions of all the atoms.
2. Polar molecular crystals have high m.p. and b.p. as compared to non-polar molecular crystals.
3. They are soft and easily compressible.
4. They are volatile in nature.
5. They are bad conductors of electricity.
6. They have low densities due to weak attractive forces.
7. They are transparent to light.

2. **Metallic Solids:**

Definition: The crystalline solids in which metal atoms are held together by metallic bonds are known as metallic solid e.g. Na, Cu etc.

Explanation (Electron Sea or Electron Gas Theory):

Metals are good conductors because the valence electrons are loosely bound. Therefore they can move from one atom to the other. Due to this mobility of electrons, they are considered to conduct electricity. The positively charged portion of the metallic atom is surrounded by electrons in such a way that these electrons serve as an atmosphere of distributed charges. The positively charged particles are immersed in it. Such an atmosphere is called an electron gas or sea. This is shown below:

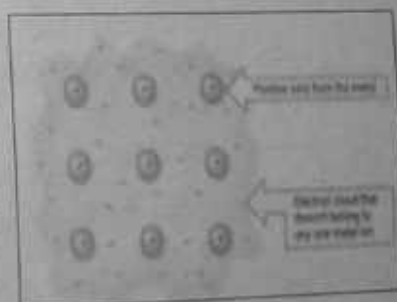


Figure 6.9 An electron sea surrounding cations

There are two forces responsible for the metallic bond.

- 1) Force of attraction between the electron gas and the positive ions.

The student should be guided to discuss and explain information.

- 2) Force of repulsion between positively charged ions. These forces are equal and opposite. Therefore, they counterbalance each other. Thus the metallic atom is neutral as a whole.

Properties:

- They are best conductors of heat and electricity.
- They have lustrous surfaces.
- They are malleable and ductile.
- They have high melting points.

Comparison of molecular crystals and metallic solids

Molecular Crystals	Metallic Solids
1. Those solid substances in which the particles forming the solids are polar or non-polar molecules are called molecular crystals e.g. Ice etc.	1. The crystalline solid in which metal atoms are held together by metallic bonds are known as metallic solids e.g. Na, Cu etc.
2. Two types of intermolecular forces hold them together. (i) Dipole-Dipole interactions (Polar) e.g. Ice, Sugar. (ii) London dispersion forces (Non-Polar) e.g. I ₂ , S ₈ , P ₄ etc.	2. In metallic crystals, electron gas theory is involved.  An electron sea surrounding cations
3. They are bad conductors of electricity because they have not free electrons.	3. They are good conductors of electricity due to presence of free electrons.
4. They are not malleable and ductile.	4. They may be malleable and ductile.

6.5.6 Hygroscopic Salts

Some salts absorb moisture from atmosphere. Such salts are called hygroscopic salts. Calcium chloride (CaCl_2) has the property of absorption of moisture from the atmosphere. Thus it becomes hygroscopic. The absorption of moisture becomes maximum when there is humidity in air. The water molecules absorbed will become part of crystal of CaCl_2 and may be called as water of crystallization such substances are called Hydrates. CaCl_2 can absorb a maximum of $2\text{H}_2\text{O}$. Therefore CaCl_2 becomes $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The water of crystallization attached will increase the mass of calcium chloride.

The student should be guided to examine the different aspects of concepts.

HOW TO GET SODIUM CHLORIDE FROM SALINE SOLUTION:

Saline water (NaCl solution) contains water along with certain impurities. If saline water is allowed to freeze in freezing mixture of water, the impurities come up to the surface in the form of ice at -3.4°C leaving behind NaCl. Ice and impurities are removed from the surface leaving behind pure NaCl.

References for additional information

- Frank L. Pilar, Elementary Quantum chemistry.
- Drew H. Wolfe, Introduction to college chemistry.
- Olmsted Williams, Chemistry, The molecular Science.

**Exercise**

Choose the correct answer (MCQs).

- The temperature at which two or more than two types of crystals exist in equilibrium is called.
(a) Melting Point
(b) Transition temperature
(c) Eutectic temperature
(d) Boiling point.
- The solids in which atoms, ions or molecules have random non-repetitive three dimensional arrangements are termed as:
(a) Crystals
(b) Glasses
(c) Alloys
(d) Amalgams
- The nature of bond in diamond is
(a) Ionic
(b) Covalent
(c) Molecular
(d) Metallic
- Crystal Lattice is an arrangement of particles in
(a) One dimension
(b) Two dimensions
(c) Three dimensions
(d) Four dimensions
- Lattice energy is also called
(a) Crystal energy
(b) Ionization energy
(c) Energy of affinity
(d) Bond Energy
- When gaseous ions are allowed to form a crystal, energy
(a) is evolved
(b) is absorbed
(c) is sometimes absorbed and sometimes released
(d) has no effect
- NaF and MgO have both atomic ratio 1:1 in their crystals such property is
(a) Polymorphism
(b) Isomorphism
(c) Isotropy
(d) Allotropy



- viii. Electric current can pass through graphite in one direction but not through other direction of crystal such a property is called
(a) Allotropy (b) Anisotropy
(c) Isomorphism (d) Polymorphism
- ix. Iron acts as an electrical conductor due to
(a) Electron cloud (b) Free protons
(c) Free neutrons (d) Free ions
- x. A crystal of the purple compound Potassium Permanganate placed at the bottom of a beaker of water and the beaker left until there is no further change. What will be observed?
(a) A uniformly purple solution.
(b) A colourless liquid with the purple crystal unchanged.
(c) A purple layer below a colourless layer.
(d) A colourless layer below a purple layer.
(e) A deep purple layer below a pale purple layer.
- xi. Which of the following method is most suitable for obtaining a pure, dry sample of NaCl from a mixture of NaCl and sand?
(a) Shake the mixture with water. Filter and dry the substances on the filter paper.
(b) Shake the mixture with water. Filter and evaporate the filtrate.
(c) Shake the mixture with water and distil off the sand.
(d) Heat the mixture gently and collect the substances which boil off.
- xii. What method could be used to obtain copper from mixture of powdered copper and sodium chloride?
(a) Heating the mixture.
(b) Fractional distillation of the mixture.
(c) Passing an electric current through the mixture.
(d) Adding excess water to the mixture and filtering.
- xiii. A bottle of copper oxide has been contaminated with some sodium chloride. How can the NaCl be removed from the copper oxide?
(a) Place the mixture in a separating funnel.
(b) Heat the mixture and allow it to cool.
(c) Add water to the mixture and filter.
(d) Add aqueous AgNO_3 to the mixture.
- xiv. Lead and zinc can be separated by distillation because they have different.
(a) Boiling point (b) Densities
(c) Mass numbers (d) Reactivities.
- xv. An insoluble solid was dropped into a measuring cylinder containing 50 cm^3 of water. What will be the effect on volume of water?
(a) 15 cm^3 (b) 17 cm^3
(c) 50 cm^3 (d) 65 cm^3

xvi. The results of the accurate weighing of some crystals are as follows:

Mass of weighing bottle empty = 25.652 g

Mass of weighing bottle + crystals = 26.541 g

What is the mass of the crystals?

(a) 0.111 g

(b) 0.889 g

(c) 1.111 g

(d) 1.889 g

xvii. The spontaneous mixing of particles is called:

(a) Evaporation

(b) Sublimation

(c) Diffusion

(d) Boiling

Write brief and short answers to the following:

i. Indicate the effect of pressure and temperature on solids.

ii. Differentiate between amorphous solids and crystalline solids.

iii. Write a note on Anisotropy.

iv. What is symmetry, symmetry operations, planes of symmetry and symmetry elements?

v. Write a note on transition temperature?

vi. What do you know by a Unit Cell?

vii. What do you know about Hexagonal Closest Packing?

viii. What do you know about Lattice Energy?

ix. Write a note on Dispersion Effect.

x. There are some changes in matter.

(i) Solids $\rightarrow$ Liquid

(ii) Liquid $\rightarrow$ Gas

(iii) Gas $\rightarrow$ Liquid

(iv) Liquid $\rightarrow$ Solid

Which of the changes require us to provide energy and which gives out energy?

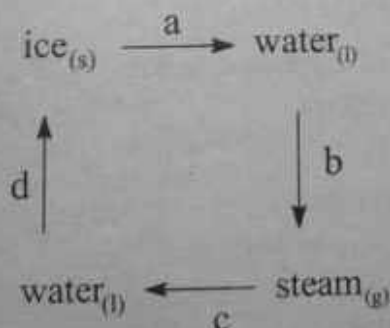
xi. Explain each of the statements below,

(a) You can smell a fish from across the road.

(b) Sugar dissolves faster in hot water than in cold water.

(c) Condensation occurs on the inside of your windows in winter.

xii. Use the following words to label the changes "a" to "d" condensation, evaporation, freezing, melting.



xiii. Look at the densities in the table below:

No	Element	Density (g/cm^3)
1	Oxygen	0.00133 at room temperature and pressure
2	Sulphur	8.92
3	Potassium	7.14
4	Nitrogen	0.00117 at room temperature and pressure

- What is the physical state of each element in the above table at 25°C ?
- Give the reason for big differences in the densities of elements shown above?
- Why is the temperature and pressure important when giving the density of oxygen and nitrogen?

xiv. Explain why the particles in solid ice stick together and those of steam do not (even when they get very close (collision)?

xv. When long bridges are constructed, the roadbed is made in sections with spaces between the sections. Why must be done so?

xvi. Explain each of the following situations in terms of energy produced or used.

- You feel cold immediately after getting out of a swimming pool, but you feel comfortably warm when you have dried yourself.
- Skin exposed for just a short time to steam can suffer severe burns whereas skin exposed to hot water for the same length of time suffers only a mild burn or none at all.

xvii. Write notes on (i) Amorphous solids (ii) Crystalline solids.

3 (a) How will you define a crystalline solid?

(b) Explain the kinetic molecular interpretation of a solid, keeping in view the following properties:

- Rigidity
- Collision
- Geometric shape
- Attractive forces

4 Define and explain compressibility (β)?

5 Define the co-efficient of expansion (α)?

6 Describe the following properties of crystalline solids:

- Cleavage plane
- Melting point
- Isomorphism
- Polymorphism
- Allotropy
- Transition temperature

✓ Differentiate between the following pairs:

- Crystalline solids and amorphous solids.
- Lattice and crystal lattice.
- Polymorphism and isomorphism.

6. Solids

185

- (d) Hexagonal closest packing and cubic closest packing.
- 8 (a) Define a unit cell. List the factors on which a unit cell depends?
- (b) Explain the structure of NaCl, keeping in view the unit cell?
- 9 Explain the three factors that affect the shape of an ionic crystal?
- 10 (a) Define lattice energy and give a particular example?
- (b) Explain the low density and high heat of fusion of ice?
- 11 Compare molecular crystals and metallic crystals.
- 12 Illustrate the conductivity of a metallic crystal using "electron sea theory".
- 13 Write a detail note on ionic solids.
- 14 (a) Define covalent crystals and give their properties?
- (b) How will you explain the covalent solids?
 - (i) When the atoms are jointly held together like diamond.
 - (ii) When the atoms have separate layers like graphite.
- 15 Value the significance of a unit cell to tell the shape of a crystal, using NaCl as an example?
- 16 ✓ Diamond is non-conductor while graphite is conductor in nature. Defend this statement.
- 17 Explain the kinetic energy of solids, based upon the kinetic molecular theory?
- 18 How will you explain the use of oxygen and sulphur to define allotropes?
- 19 ✓ A compound like CaCl_2 (calcium chloride) fluctuate in mass from day to day because of humidity. Evaluate this statement *hygroscopic*.
- 20 Saline water can be purified by repeated freezing method. Justify it.



7

CHEMICAL EQUILIBRIUM



After completing this lesson, you will be able to:

- Define chemical equilibrium in terms of a reversible reaction.
- Write both forward and reverse reactions and describe the macroscopic characteristics of each.
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
- Describe the microscopic events that occur when a chemical system is in equilibrium.
- Write the equilibrium expression for a given chemical reaction.
- Relate the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction.
- Define and explain solubility product.
- Write expression for reaction quotient.
- Determine if the equilibrium constant will increase or decrease when temperature is changed, given the equation for the reaction.
- Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.
- State Le Chatelier's Principle and be able to apply it to systems in equilibrium with changes in concentration, pressure, temperature, or the addition of catalyst.
- Define and explain common ion effect giving suitable examples.
- Explain industrial applications of Le Chatelier's Principle using Haber's process as an example.

Reading

INTRODUCTION

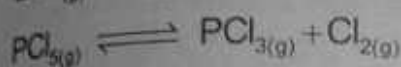
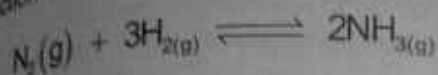
When we presented stoichiometry in Chapter – 1, we described that reactions proceed virtually to completion when the limiting reactant is completely consumed. This is true for reactions that virtually go to completion i.e., reactants are completely consumed and converted into the products. Such reactions are called irreversible reactions. Such reactions stop when the limiting reactant is consumed. However in many reactions the net formation of products comes to an end before all the limiting reactant has been consumed. Such reactions actually proceed in both the directions i.e. forward and backward and are called reversible reactions. These reactions reach at a stage called chemical equilibrium. At this stage the concentration of reactants and

products become constant. But the reaction continues to proceed in both the directions without any change in concentration of reactants and products under existing conditions. Such reactions never go to completion and are called reversible reactions.

In this chapter we will discuss how and why a chemical reaction comes to equilibrium. We will discuss the principles and applications of chemical equilibrium.

7.1 REVERSIBLE REACTIONS AND DYNAMIC EQUILIBRIUM

A reversible reaction is one in which the products once formed can react to form reactants. Such reactions do not go to completion even if stoichiometric amounts of the reactants are taken. These reactions take place both in the forward and backward directions under the existing conditions. Some examples of reversible reactions are given below: which reaction is forward reaction?



The double arrow $\rightleftharpoons$ tells that the reaction is reversible.

Consider the reaction between steam and carbon monoxide under appropriate conditions. On mixing macroscopic changes are observed (e.g. changes in concentration).

Suppose that the reaction is started with same number of moles of both the reactants.

When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur. Therefore the forward reaction has its maximum speed at the beginning. This leads to a decrease in the concentration of the reactants.



As H_2O and CO are gradually used up, the forward reaction gradually slows down. As the molecules of H_2 and CO_2 accumulate reverse reaction also starts. With the increase in concentration of H_2 and CO_2 more and more collisions per second between these molecules occur. Therefore reverse reaction proceeds with increasing speed. This means that forward reaction starts with maximum speed and gradually slows down, whereas the reverse reaction starts at zero speed and gradually increases its speed.



Eventually a time comes when both reactions proceed at the same speed. The reaction at this stage is said to be in chemical equilibrium. The concentration of reactants and products become constant.



Unless the system is somehow disturbed no further changes in concentration will occur. "The state of a reversible reaction at which composition of the reaction mixture does not change is called the state of chemical equilibrium. The

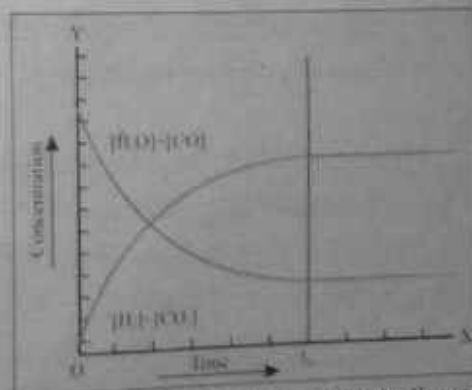


Figure 7.1: The plots of concentration of reactants and products versus time

The student should be guided to identify forward and reverse reactions and explain state of equilibrium.

plots of the concentrations of reactants and products versus time are shown in Fig. 7.1. What do these plots show? Why have they become parallel?

Since the concentration of reactants and products become constant it may appear that the reaction has stopped. But this is not true. On the microscopic level there is excited activity. Individual molecules of reactants continue to combine. Individual molecules of products also continue to combine. But the rate of one process is exactly balanced by the rate of the other. Therefore this is a dynamic equilibrium. The system is dynamic because individual molecules react continuously, but the rate of the forward and reverse reactions are equal. It is at equilibrium because no net change occurs.

7.1.1 The Equilibrium Constant

Two chemists C.M Guldberg and P. Wage in 1864 proposed the law of mass action as a general description of the equilibrium state. This Law you have learnt in a grade IX-X.

It states that "the rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances". It can also be defined as "the rate of chemical reaction is proportional to the product of molar concentration of each reacting substance raised to a power equal to its stoichiometric coefficient in the balanced chemical equation. The term active mass means, the concentration of the reactants and products in moles dm^{-3} for a dilute solution.

Consider the following general reversible reaction.



Where A, B, C and D represent chemical species and a, b, c and d are their coefficients in the balanced equation.

According to the law of mass action.

$$\begin{aligned} \text{Rate of forward reaction, } R_f &\propto [A]^a [B]^b \\ &= k_f [A]^a [B]^b \end{aligned}$$

Where k_f is the rate constant for the forward reaction.

$$\begin{aligned} \text{Rate of reverse reaction, } R_r &\propto [C]^c [D]^d \\ &= k_r [C]^c [D]^d \end{aligned}$$

Where k_r is the rate constant for the reverse reaction.

At equilibrium state

$$\text{Rate of forward reaction} = \text{Rate of reverse reaction}$$

Thus

$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

On rearranging

$$\frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

(3)

$$\text{Where } K_c = \frac{k_f}{k_r}$$

and is known as equilibrium constant, and the equation (3) is known as equilibrium constant expression. The square brackets indicate the concentration of the chemical species at equilibrium. Concentration of which species are taken in the numerator in K_c expression?

Thus the equilibrium constant expression for any reaction can be written from its balanced equation. Concentration of products are taken in the numerator and concentration of reactants in the denominator.

Conditions for Equilibrium

Important features of equilibrium constant expression are as follows:

- K_c applies only at equilibrium. The subscript c indicates the concentration of reactants and products in moles per dm^3 at equilibrium state.
- K_c is independent of initial concentration of reactants and products but depends upon temperature. At a given temperature, it has only one value. Whether we start reaction with pure reactants or pure products or any composition in between, the value of K_c remains unchanged.
- K_c is related to the coefficients of the balanced chemical equation. The concentration of the products are placed in the numerator and those of reactants in the denominator. Each concentration is raised to a power equal to its coefficient in the balanced chemical equation.
- The magnitude of K_c indicates the position of equilibrium. When K_c is less than 1, the denominator is greater in magnitude than the numerator. This means the concentration of the reactants are greater than those of products when the equilibrium is established. Whereas, when K_c is greater than 1, the numerator is greater in magnitude than the denominator. This means the concentration of the products are greater than those of the reactants at equilibrium.

It is important to recognize the difference between the equilibrium constant expression and rate law of a reaction. You will learn about rate law expression in chapter on chemical kinetics. In both these expressions, concentration terms are raised to powers. The rate law describes how the rate of a reaction changes with concentration. It cannot be written from the balanced chemical equation. Whereas the equilibrium expression describes the concentration of reactants and products when the net rate of reaction is zero. It can be written from a balanced chemical equation.

7.1.2 Examples of Equilibrium Constant Expression

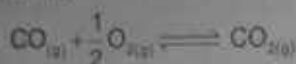
Problem solving strategy

1. Write products in the numerator and reactants in the denominator in square brackets.

2. Raise each concentration to the power that correspond to the co-efficient of each species in the balanced chemical equation.

Example 7.1

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

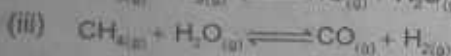
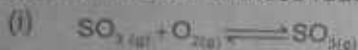
Example 7.2

$$K_c = \frac{[\text{CO}_2]}{[\text{CO}][\text{O}_2]^{1/2}}$$

**Self Check Exercise 7.1**

The following equations represent various industrial reactions at equilibrium. Write K_c

1. Expression for each of these reactions. Do not forget to balance the equations:



2. Give the balanced equations that correspond to following equilibrium expressions.

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

$$K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]}$$

7.1.3 Units of Equilibrium Constant**Problem solving strategy**

1. Write equilibrium constant expression.

2. Write mol dm^{-3} as units of concentration of each species within square brackets.

3. Simplify the expression.

Equilibrium constant may or may not have units. Equilibrium constant has no units if the number of moles of the reactants are equal to the number of moles of the products. For instance K_c for the following reaction has no units.



$$K_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]}$$

$$K_c = \frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \text{No units}$$

7. Chemical Kinetics

units. For example



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

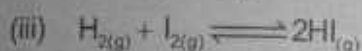
$$K_c = \text{mole dm}^{-3}$$

In this way we can determine the units for K_c . However units of equilibrium constant is not usually written.



Self Check Exercise 7.2

Determine the units for K_c for the following reactions:



The value of K_c at a given temperature can be calculated if we know the equilibrium concentration of the reaction components.

Example 7.3

The following equilibrium concentrations were observed for the reaction at 500°C .



$$[\text{A}] = 0.399\text{M}, [\text{B}] = 1.197\text{M}, [\text{AB}] = 0.203\text{M}$$

Calculate K_c

Solution

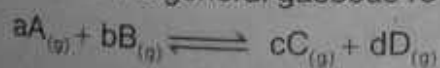
$$K_c = \frac{[\text{AB}]^2}{[\text{A}][\text{B}]^3}$$

$$K_c = \frac{(0.203 \text{ mol dm}^{-3})^2}{(0.399 \text{ mol dm}^{-3})(1.19 \text{ mol dm}^{-3})^3}$$

$$= 6 \times 10^{-2} \text{ dm}^6 \text{ mole}^{-2}$$

7.1.4 Equilibrium Expressions Involving Partial Pressure, Number of Moles and Mole Fraction.

Consider the general gaseous reversible reaction.



The student should be guided to use information to solve different data.

For gases the expression is often expressed in terms of partial pressure of each gas. According to Henry's law "At constant temperature, the partial pressure of a gas is directly proportional to its molar concentration."

Equilibrium constant K_p in term of partial pressures is given by:

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

Where P_A , P_B , P_C and P_D are partial pressures of gas A, B, C and D respectively K_p is related with K_c by the following equation.

$$K_p = K_c (RT)^{\Delta n} \quad \Delta n = n_p - n_r$$

Where Δn is the difference between the total number of moles of the products and the reactants.

When equilibrium concentrations of reactants and products are expressed in terms of their moles, the equilibrium constant is represented by K_n and is given by the following equation.

$$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

Where n_A , n_B , n_C and n_D are the moles of A, B, C and D respectively at the equilibrium state. K_p is also related with K_n .

$$K_p = K_n \left(\frac{P}{N} \right)^{\Delta n}$$

Where P is the pressure of reaction mixture at equilibrium and N is the total number of moles of reactants and products as shown by the balanced equation.

When the equilibrium concentration of the reactants and products are expressed by their mole fractions, the equilibrium constant is represented by K_x and is given by the following equations.

$$K_x = \frac{x_C^c \times x_D^d}{x_A^a \times x_B^b} \quad x_C = \frac{n_C}{n_T}$$

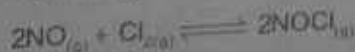
Where x_A , x_B , x_C and x_D are mole fractions of A, B, C and D respectively. K_p is related with K_x by the following expression.

$$K_p = K_x (P)^{\Delta n}$$

Where P is the pressure of the equilibrium mixture.

Example 7.4

Following reaction was studied at 25°C. Calculate its K_p and K_c .



The partial pressures at equilibrium were found to be

$$P_{\text{NOCl}} = 1.2 \text{ atm}$$

$$P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm}$$

7. Chemical Kinetics

$$\text{PCl}_2 = 3.0 \times 10^{-1} \text{ atm}$$

Problem Solving Strategy

1. Write K_p expression
2. Substitute the partial pressures of each species.
3. Simplify to get K_p .
4. Calculate Δn
5. Write expression relating K_p and K_c
6. Substitute known values in it and find K_c

$$K_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})^2 (P_{\text{Cl}_2})}$$

$$K_p = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2 (3.0 \times 10^{-1})}$$

$$K_p = 1.9 \times 10^3$$

Now

$$K_p = K_c (RT)^{\Delta n}$$

$$\Delta n = 2 - (2 + 1) = -1$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$$

$$T = 25^\circ\text{C} + 273 = 298\text{K}$$

$$K_p = K_c (RT)^{\Delta n}$$

$$1.9 \times 10^3 = K_c (0.0821 \times 298)^{-1}$$

$$1.9 \times 10^3 = \times \frac{K_c}{(0.0821 \times 298)}$$

$$K_c = 1.9 \times 10^3 \times 0.0821 \times 298$$

$$K_c = 4.65 \times 10^4$$



Self Check Exercise 7.3

The contact process prepares purest sulphuric acid commercially. Following reaction takes place in the contact chamber in the presence of V_2O_5 .



Calculate K_p if the following concentrations are found at equilibrium.

$$[\text{SO}_2] = 0.59\text{M}, [\text{O}_2] = 0.05\text{M} \text{ \& \; } [\text{SO}_3] = 0.259\text{M}$$

(Ans: 0.1576)

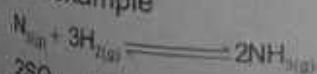
7.1.5 Types of Equilibrium

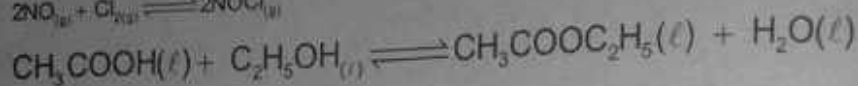
With respect to the physical states of reactants and products, there are two types of Chemical Equilibrium.

Homogeneous Equilibria

An equilibrium system in which all of the reactants and products are in the same phase.

For example





ii. Heterogeneous Equilibria

Equilibria which involve more than one phases are called Heterogeneous equilibria. For example

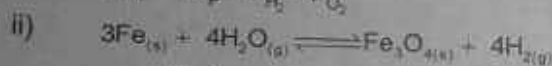


If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is because the change in concentration of any pure solid or liquid has no effect on the equilibrium system.



$$K_c = [\text{H}_2]^2 [\text{O}_2]$$

$$\text{and } K_p = P_{\text{H}_2}^2 \times P_{\text{O}_2}$$



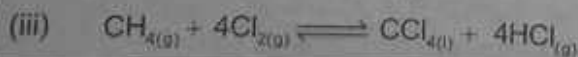
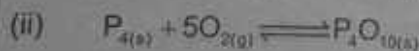
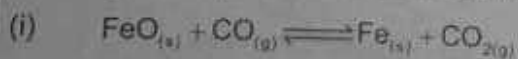
$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

$$\text{and } K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$



Self Check Exercise 7.4

Write K_c and K_p expressions for each of the following reactions.



7.1.6 Ways to Recognize Equilibrium and Determination of Equilibrium Constant

Equilibrium constant expression can be determined by physical as well as chemical methods.

a) Physical Method (spectrometric method)

This method is based on the measurement of a physical property of the reaction mixture. This physical property is measured during the course of reaction without removing the sample



The student should be guided to operate the following information in practical uses.

7. Chemical Kinetics

175

from the reaction mixture. We will discuss spectrometric method. This method is applicable if a reactant or product absorbs ultraviolet, visible or infrared radiation. The concentration can be determined by measuring the amount of radiation absorbed. Equilibrium constant for $N_2O_4 - NO_2$ system can be determined by the spectrophotometer.



N_2O_4 is a colourless gas whereas NO_2 is reddish brown gas. The progress of the reaction can be studied by measuring the absorbance at regular intervals. Absorbance is proportional to the concentration of NO_2 . At equilibrium spectrometer will show constant value of absorbance. Suppose reaction is started with "a" moles of N_2O_4 at $100^\circ C$. and x moles of it, is converted to NO_2 . By applying stoichiometry, the amount of NO_2 present in equilibrium will be $2x$, which is measured by the spectrophotometer. Suppose the volume of the reaction mixture is $V \text{ dm}^3$, then we can write.

	$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$	
Initial Conc. (in moles)	a	zero
Eq. Conc. (in moles)	$a - x$	$2x$
Eq. Conc. (moles/dm ³)	$\frac{a - x}{V}$	$\frac{2x}{V}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a - x}{V}\right)}$$

$$K_c = \frac{4x^2}{(a - x)V}$$

Example 7.5

At $100^\circ C$, 0.1 mole of N_2O_4 is heated in a one dm³ flask. At equilibrium concentration of NO_2 was found to be 0.12 moles. Calculate K_c for the reaction.

Problem Solving Strategy

1. Write equilibrium reaction.
2. Write initial conc. of each species below equilibrium reaction.
3. Work out equilibrium conc. of each species.
4. Use equilibrium conc. of each species in K_c expression and find K_c .

Solution

$$[NO_2] = 0.12 \text{ mole}$$

Since one mole of N_2O_4 gives 2 moles of NO_2

$$2x = 0.12$$

$$X = \frac{0.12}{2}$$

$$X = 0.06$$

$$[N_2O_4] = 0.1 - 0.06$$

$$= 0.04 \text{ mole}$$

	$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$	
Initial Conc.	0.1	zero
(in moles)		
Eq. Conc.	$0.1 - 2x$	0.12
(in moles)		
Eq. Conc.	$\frac{0.04}{1}$	$\frac{0.12}{1}$
(mole/dm ³)		
	0.04	0.12

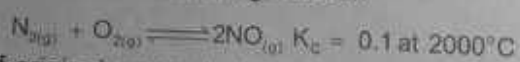
$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(0.12)^2}{(0.04)}$$

$$K_c = 0.36$$

Example 7.6

Consider the following reaction



If original concentrations of N_2 and O_2 were 0.1M each. Calculate the concentrations of NO at equilibrium.

Solution

	$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$		
Initial Conc.	0.1M	0.1M	0
Eq. Conc.	(0.1 - X)	(0.1 - X)	2X
(mole/dm ³)			

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$0.1 = \frac{(2X)^2}{(0.1 - X)(0.1 - X)}$$

Taking square root of both the sides

$$0.32 = \frac{2X}{0.1 - X}$$

$$X = 0.014M$$

$$[N_2] = [O_2] = 0.1 - X$$

$$= 0.1 - 0.014$$

$$= 0.086M \text{ each}$$

$$[NO] = 2X$$

$$= 2 \times 0.014$$

$$= 0.028 M$$



Self Check Exercise 7.5

For the reaction



$K_c = 0.60$ at 500°C . If a mixture of 0.30M of each H_2 and CO_2 is heated at 500°C , calculate the concentration of CO at equilibrium.

b) Chemical Method

In this method, the amount of a reactant or product is determined by a suitable chemical reaction. Consider the reaction between acetic acid and ethanol to form ethyl acetate and water. It is an example of reversible reaction in the solution state.



Suppose this reaction is started by taking 'a' moles of acetic acid and 'b' moles of ethanol in a stoppered flask at room temperature. A small amount of mineral acid is added in the mixture to catalyse the reaction.

The progress of the reaction can be studied by determining the concentration of acetic acid after regular intervals. For this purpose small portion of mixture is withdrawn. The concentration of acetic acid is determined by titrating it against a standard solution of NaOH using phenolphthalein as indicator. Concentration of acetic acid will decrease until equilibrium is attained. Suppose x moles of acetic acid has reacted with ethanol. Since one mole of acetic acid reacts with one mole of ethanol, the amount of ethanol reacted with acetic acid will also be x moles. As one mole of each of the product is formed. At equilibrium x moles of ethyl acetate and x moles of water are produced. This data is shown in table 7.1

Table 7.1. Data for the equilibrium reaction between acetic acid and ethyl alcohol.

Reaction	$\text{CH}_3\text{COOH}(\ell) + \text{C}_2\text{H}_5\text{OH}(\ell) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\ell) + \text{H}_2\text{O}(\ell)$			
Initial	a	b	Zero	Zero
Conc				
(in moles)				
Eq. Conc	a - x	b - x	x	x
(in moles)				

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$K_c = \frac{(x)(x)}{(a-x)(b-x)}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

Example 7.7

When 60g of acetic acid and 46g of ethyl alcohol are heated to give an equilibrium mixture of 12g water and 58.7g of ethyl acetate are formed. Find K_c for the reaction.

$$\text{Initial moles of } \text{CH}_3\text{COOH} = \frac{60\text{g}}{60\text{g/mole}} = 1 \text{ mole}$$

$$\text{Initial moles of } \text{C}_2\text{H}_5\text{OH} = \frac{46\text{g}}{46\text{g/mole}} = 1 \text{ mole}$$

At equilibrium

$$\text{Moles of } \text{CH}_3\text{COOC}_2\text{H}_5 = \frac{58.7\text{g}}{88\text{g/mole}} = 0.666 \text{ mole}$$

$$\text{Moles of } \text{H}_2\text{O} = \frac{12\text{g}}{18\text{g/mole}} = 0.666 \text{ mole}$$



Init. conc
(in moles)

1 1 0 0

Eq. conc.
(moles)

1 - 0.666 1 - 0.666 0.666 0.666
0.333 0.333

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$K_c = \frac{(0.666)(0.666)}{(0.333)(0.333)}$$

$$K_c = 4$$

**Self Check Exercise 7.6**

1. When dissolved in water, glucose and fructose exists in equilibrium as follows:



An analyst prepared a 0.25M fructose solution at room temperature. At equilibrium he found that its concentration decreased by 0.038M. Calculate K_c for the reaction. (Ans: 0.179)

3. When 3.88 moles of NO and 0.88 moles of CO_2 were heated in a flask at a certain temperature. At equilibrium 0.11 moles of each of the product were present. Calculate K_c for the reaction.



(Ans: 0.0042)

7.1.7 Applications of the Equilibrium Constant

Equilibrium constant for a reaction can be used to predict many important features of the reactions. For instance, it can be used to predict (1) Direction of the chemical reaction (2) Extent of the chemical reaction (3) Effect of changes in condition of the chemical reaction on the equilibrium position and equilibrium constant.

The Direction of a Reaction

The direction of reaction when reactants and products of a given chemical reaction are mixed, it is important to know whether the mixture is at equilibrium and if not, in which direction it will move to achieve equilibrium state. For this purpose we use the reaction quotient (Q). The ratio of concentration of products to reactant at any particular time is called reaction quotient. It is obtained by applying the law of mass action, using initial concentration or concentration at any particular time instead of equilibrium concentration.

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]}$$

The value Q leads to one of the following possibilities.



This indicates that more product is needed to acquire equilibrium. Therefore system must shift to the right until equilibrium is attained.



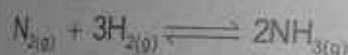
This indicates that less product or more reactant is needed to acquire equilibrium. Therefore system must shift to the left until equilibrium is reached.



This shows that reaction is at equilibrium. No shift will occur.

Example 7.8

For the synthesis of ammonia at 500°C , $K_c = 6.0 \times 10^{-1}$



Predict the direction in which the system will shift to attain equilibrium when the concentration of species were found to be

$$[\text{H}_2] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{N}_2] = 1.0 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3] = 1.0 \times 10^{-3} \text{ M}$$

Problem Solving Strategy

1. Write the reaction quotient expression for the reaction

2. Substitute the given values of conc. of each species in the expression and find Q

3. Compare Q with K_c . If Q is $> K_c$, the system will shift to the left to achieve equilibrium.

Solution

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$Q = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-3})(1.0 \times 10^{-2})^3}$$

$$Q = 1.0 \times 10^3$$

But

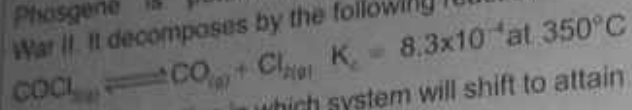
$$K_c = 6.0 \times 10^{-1}$$

Therefore $Q > K_c$. The system will shift to the left to achieve equilibrium.



Self Check Exercise 7.7

Phosgene is a potent chemical warfare agent and has been used in World War I. It decomposes by the following reaction.



Predict the direction in which the system will shift to attain equilibrium, when the concentrations of the species were found to be

$$[\text{COCl}_2] = 0.5 \text{ M}$$

$$[\text{CO}] = 2.5 \times 10^{-2} \text{ M}$$

$$[\text{Cl}_2] = 2.5 \times 10^{-2} \text{ M}$$

(Ans: Towards left)

ii. The Extent of Chemical Reaction

The extent of a chemical reaction can be predicted by considering the magnitude of the equilibrium constant. Again there are three possibilities.

a. K_c is very large

Many reactions have a very large equilibrium constant, for example



If the concentration of each of the reactants at equilibrium is 1 mole then the concentration of HBr would be

$$\frac{[\text{HBr}]^2}{[1] \times [1]} = 5.4 \times 10^{18}$$

$$[\text{HBr}] = \sqrt{5.4 \times 10^{18}}$$

$$= 2.32 \times 10^9 \text{ M}$$

$$K_c = \frac{[\text{P}]}{[\text{R}]}$$

It means that the concentration of HBr is very large as compared to that of reactants. At equilibrium, the mixture will have mainly products. Thus, a large value of K_c indicates that the reaction goes virtually to completion.

b. K_c is very small

Reactions having a very small K_c do not proceed appreciably in the forward direction. For example,



$$K_c = 1.0 \times 10^{-30} \text{ at } 25^\circ\text{C}$$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 1.0 \times 10^{-30}$$

If one mole of each of the reactants is present at equilibrium, then the concentration of NO would be

$$\frac{[\text{NO}]^2}{1 \times 1} = 1 \times 10^{-30}$$

$$[\text{NO}] = \sqrt{1 \times 10^{-30}}$$

$$[\text{NO}] = 1 \times 10^{-15} \text{ moles}$$

Thus concentration of NO will be very small. Equilibrium mixture will have mainly reactants. Therefore, small value of K_c indicates that the reaction has very little tendency to move in the forward direction.

K_c is neither very small nor very large

When K_c is neither very small nor very large, the equilibrium mixture contains appreciable amounts of both products and reactants. For example:



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.36$$

If 1 mole of N_2O_4 is present at equilibrium, 0.6 mole of NO_2 will be present in the equilibrium mixture. Hence the equilibrium mixture will contain appreciable amount of reactants and products. In such cases neither forward nor the reverse reaction go to completion.



Self Check Exercise 7.8

White phosphorus P_4 is produced by the reaction of phosphorite rock, $\text{Ca}_3(\text{PO}_4)_2$ with coke. When exposed to air it bursts into smoke and fumes and releases a large amount of heat. Predict whether K_c for this reaction is large or small.



7.2 FACTORS AFFECTING EQUILIBRIUM

It is necessary to understand the factors that control the position of a chemical equilibrium. A knowledge of such factors help industrial chemists to choose conditions which favour desired product as much as possible. We can predict the effect of various factors such as concentration, pressure and temperature on a system at equilibrium by using Le Chatelier's principle. **"It states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction which tends to reduce that change".**

7.2.1 The Effect of a Change in Concentration

When the concentration of one or more of the reactants or products present in equilibrium mixture is disturbed, the system will not remain at equilibrium state. According to Le Chatelier's principle, the equilibrium shifts to accommodate the substance added or removed and restore equilibrium again.

Consider the following gas phase equilibrium:



The student should be guided to demonstrate this knowledge in various ways.

When CO_2 is added to this equilibrium system, it is no longer in equilibrium. High concentration of CO_2 increases the rate of forward reaction relative to the reverse reaction. Thus more CO_2 and H_2 combine and more CO and H_2O form. As time passes the concentration of CO_2 and H_2 decrease, lowering the rate of forward reaction. At the same time increase in concentration of the products accelerate the reverse reaction ultimately the two rates become equal again and equilibrium is re-established. At the new equilibrium concentration of CO and H_2O are higher than were present before the CO_2 was added. Thus equilibrium is said to have shifted to the products side.

In all chemical systems, an increase in concentration of any reactant shifts the equilibrium towards the formation of the products. If concentration of a product is increased, the equilibrium shifts towards the reactants. A shift towards the reactant lowers the concentration of the added product.

The opposite happens when we decrease the concentration of a reactant or product. If the reactant concentration is decreased, the equilibrium system shifts towards the reactants. Removal of product shifts equilibrium towards the products. Let us understand the microscopic events that take place in an equilibrium system. The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules. At equilibrium the number of effective collisions for the forward and reverse reactions are equal. Increase in concentration of reactant increases such collisions for the forward reaction. Thus equilibrium shifts towards right with the formation of more molecules of products. Number of effective collisions for the reverse process also increase. As time passes the effective collisions of reactant molecules decrease lowering the rate of forward reaction. Ultimately the number of effective collisions for both processes again become equal and equilibrium is re-established.

Example 7.9

K_c for the following reaction is 1.0×10^{-3} at 230°C



1.6 moles of ICl , 0.05 mole of I_2 and 0.05 mole of Cl_2 is present in the equilibrium mixture in 2dm^3 container at 230°C . Determine the equilibrium concentrations of I_2 , Cl_2 and ICl when the equilibrium is restored after the addition of another mole of ICl .

Solution

On adding one mole of ICl into the equilibrium mixture will shift equilibrium in the forward direction. Thus the concentration of ICl will decrease and concentration of I_2 and Cl_2 will increase by x whereas concentration of ICl will decrease by $2x$.

	$2\text{ICl}_{(g)}$	$\rightleftharpoons$	$\text{Cl}_{2(g)}$	$+$	$\text{I}_{2(g)}$
Initial Conc. (in moles)	$1.6 + 1 = 2.6$		0.05		0.05
Conc. at new Equilibrium (in moles)	$2.6 - 2x$		$0.05 + x$		$0.05 + x$

$$\frac{2.6 - 2x}{2}$$

$$\frac{0.05 + x}{2}$$

$$\frac{0.5 + x}{2}$$

$$K_c = \frac{[Cl_2][I_2]}{[ICl]^2}$$

$$1.0 \times 10^{-3} = \frac{\left(\frac{0.05 + x}{2}\right)\left(\frac{0.05 + x}{2}\right)}{\left(\frac{2.6 - 2x}{2}\right)^2}$$

Taking square root of both the sides

$$\sqrt{1.0 \times 10^{-3}} = \frac{\left(\frac{0.05 + x}{2}\right)}{\frac{2.6 - 2x}{2}}$$

$$3.1 \times 10^{-2} = \frac{0.05 + x}{2.6 - 2x}$$

$$x = 0.029 \text{ moles dm}^{-3}$$

$$[ICl] = 2.6 - 2x$$

$$= 2.6 - 2 \times 0.029$$

$$= 2.571 \text{ moles dm}^{-3}$$

$$[I_2] = [Cl_2] = 0.05 + x$$

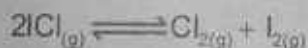
$$= 0.05 + 0.029$$

$$= 0.079 \text{ moles dm}^{-3}$$



Self Check Exercise 7.9

K_c for the following reaction is 1.0×10^{-3} at 230°C



1.6 moles of ICl , 0.05 mole of I_2 and 0.05 mole of Cl_2 is present in the equilibrium mixture in 2dm^3 container at 230°C . Determine the equilibrium concentrations of I_2 , Cl_2 and ICl when the equilibrium is restored after the removal of one mole of ICl . (Ans: 0.0208M, 0.0208M, 0.658M)

Do you know?

Cigarette smoke is a major source of CO. Smokers inhale it directly through burning cigarette, even non-smoker also inhale CO when they are exposed to cigarette smoke of others. CO combines with hemoglobin to form carboxy-hemoglobin. Because carboxy-hemoglobin is unable to transport oxygen, the heart must pump more blood to get the needed oxygen. Also heavy smokers do not give their hemoglobin much opportunity to recover. Thus chronic exposure to CO from smoking is believed to cause heart disease and heart attacks. Other substances in cigarette smoke can cause lung cancer and respiratory problems. Infact, smoking is a habit with many higher risks.

7.2.2 The Effect of Pressure Change

Equilibria that contain gases are influenced by pressure changes. When pressure on a gaseous system at equilibrium is increased, the system tends to reduce the volume to undo or minimize the effect of increased pressure. This is done by decreasing the total number of gaseous molecules in the system. This is because at constant temperature and pressure, the volume of a gas is directly proportional to the total number of molecules of the gas present.

Consider the following equilibrium system. Which side contains smaller numbers of molecules?



If we suddenly increase pressure on the system, what will happen to the equilibrium position? The reaction system will reduce its volume by reducing the number of molecules present. This means that the reaction will shift to the right, because in this direction three molecules (two of SO_2 and one of O_2) react to produce two molecules (of SO_3), thus reducing the total number of gaseous molecules present. This means the equilibrium position will shift towards the side involving the smaller number of gaseous molecules in the balance chemical equation.

When the pressure is reduced the system will shift so as to increase its volume.

There are certain equilibria in which the total number of molecules are same on either side. For example



Whenever the pressure is changed on such a system, neither forward nor the reverse reaction is favoured because the number of molecules is the same on each side. Such equilibria are not affected by pressure or volume changes.



Self Check Exercise 7.10

The formation of methanol is an important industrial reaction in the processing of new fuels

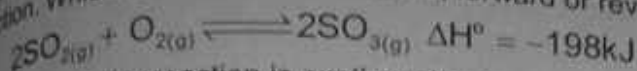


A student decreases pressure over the system in an attempt to increase the yield of methanol. Is this approach reasonable? Explain.

7.2.3 The Effect of Change in Temperature

You have already learnt in grade IX-X that chemical reactions are always associated with energy changes. Chemical reactions that liberate heat are called exothermic and those that absorb heat are called endothermic. This has also been discussed in section 11.1.4. Heat is placed on the right side of the equation in case of exothermic reactions. In endothermic reactions, it is placed on the left side of the equation. We can use Le Chatelier's Principle to predict the direction of change. Treat energy as a reactant in the endothermic process. Predict

the direction of shift in the same way as an actual reactant or product is added or removed. Therefore an increase in temperature adding heat favours the endothermic reaction and decrease in temperature (removing heat) favours the exothermic reaction. Consider the following reaction. Which reaction is endothermic, forward or reverse reaction.



Because the reaction is exothermic, we can write



$A + \text{heat} \rightleftharpoons B$ (Endothermic)
(Favourable condition)
high heat is

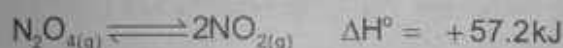
Heat can be treated as if it were a substance involved in the reaction. According to the Le Chatelier's Principle an increase in temperature will shift reaction from right to left in order to absorb the added heat and to counteract the temperature increase. As a result of this change concentration of SO_3 will decrease and concentrations of SO_2 and O_2 will increase. As a result, the value of equilibrium constant will decrease.

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \leftarrow \begin{array}{l} \text{increases} \\ \text{decreases} \end{array}$$

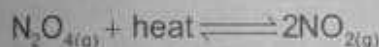
$A \rightleftharpoons B + \text{heat}$ (Exothermic)
(low heat is favourable)

That is why $K_c = 2.8 \times 10^2$ at 1000K whereas at 298K the value of $K_c = 1 \times 10^{26}$. The equilibrium production of SO_3 is favoured at lower temperature. This is because K_c is much larger at 298K than at 1000K.

Now consider the following reaction



Because the reaction is endothermic, we can write



As the temperature is increased, heat enters the system and the reaction will shift from left to right. As a result of this change, concentration of NO_2 will increase and that of N_2O_4 will decrease. This will increase the value of K_c .

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \leftarrow \begin{array}{l} \text{increases} \\ \text{decreases} \end{array}$$

That is why K_c for this reaction is 7.7×10^{-5} at 0°C and 0.4 at 100°C .

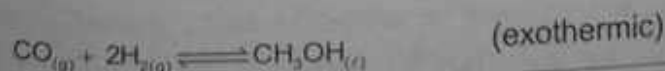


Self Check Exercise 7.11

Consider the following equilibrium



What would be the effect on the position of equilibrium when temperature is decreased?
Predict the effect of increasing the temperature on the amount of product in the following reaction.



Encourage students to demonstrate effects of change in concentration, pressure and temperature with some other examples.

7.2.4 The Effect of Addition of Catalyst

A catalyst added to a reaction mixture speeds up both the forward and the reverse reaction to the same degree. Thus catalyst has no effect on the equilibrium concentrations of reaction mixture. However, the catalyst is important in enhancing the rate at which equilibrium is established.

7.3 INDUSTRIAL APPLICATION OF LECHATLIER'S PRINCIPLE (SYNTHESIS OF AMMONIA BY HABER'S PROCESS)

For industrial processes it is important to maximise the concentration of the desired product and minimise the leftover reactants. Le Chatelier's principles and reaction kinetics can both be used to design best conditions to give the highest possible yield of the product in an economic way.

The manufacture of ammonia by Haber's process is represented by the following equation.



This equation provides the following information.

- The reaction is exothermic.
- The reaction proceeds with a decrease in number of molecules or moles.

Le Chatelier's principle suggests three ways to get maximum yield of ammonia.

i. Low Temperature

The forward reaction is exothermic therefore, low temperature will favour the formation of ammonia. The suitable temperature is 400°C .

ii. High Pressure

Since four molecules (one of N_2 and three of H_2) react to produce two molecules of NH_3 . Thus high pressure will shift the equilibrium to the right side i.e. formation of NH_3 . The most suitable pressure is 200 – 300 atm.

Thus optimum condition for equilibrium production of ammonia is low temperature and high pressure. Although at low temperature yield of ammonia is high, but the rate of its formation is so slow that the process becomes uneconomical. Therefore, a catalyst is used to increase the rate of reaction. Usually a piece of iron with other metal oxides is used as catalyst. The equilibrium mixture contains 35% NH_3 by volume.

iii. Continual removal of ammonia

A final factor which greatly increases the production of ammonia is the continuous removal of ammonia as it is formed. This is done by liquefying ammonia. The equilibrium mixture is cooled by refrigeration coils until ammonia condenses at -33.4°C and is removed. N_2 and H_2 which do not liquefy at this temperature are recycled into the reaction chamber. The stress caused by the continual removal of ammonia shifts the equilibrium toward the

The student should be guided to interpret information and appraise the importance of Le Chatelier's principle.

7. Chemical Kinetics

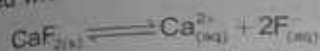
production of more ammonia. In fact the mixture need not to be allowed to come to equilibrium at all. In this way practically 100% conversion of N_2 and H_2 to NH_3 is possible.

7.4 SOLUBILITY PRODUCT AND PRECIPITATION REACTIONS

Now we will discuss some of the important equilibria which have some analytical importance.

7.4.1 Solubility Product

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and remaining compound settle at the bottom. Dynamic equilibrium is established between undissolved solid compound and its ions in the saturated solution. For example when CaF_2 is mixed with water. Following equilibrium is established.



K_c for this equilibrium can be written as

$$K_c = \frac{[Ca^{2+}][F^{-}]^2}{[CaF_2]}$$

Since CaF_2 is slightly soluble salt its concentration almost remains constant.

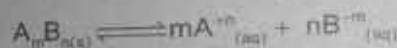
Therefore,

$$K_c [CaF_2] = [Ca^{2+}] [F^{-}]^2$$

$$K_{sp} = [Ca^{2+}] [F^{-}]^2$$

Where K_{sp} is a constant known as the solubility product constant. It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balance chemical equation.

In general, K_{sp} expression of any slightly soluble ionic compound $A_m B_n$ can be written as



$$K_{sp} = [A^{+n}]^m [B^{-m}]^n$$

This means that the solubility product constant is equal to the product of the equilibrium concentration of ions each raised to a power equal to the number of such ions in the formula unit of the compound.

7.4.2 Precipitation Reactions

In the previous section, we have considered solids dissolving in solutions. Now we will consider the reverse process i.e the formation of a solid from solution. **An aqueous reaction that takes place when two or more solution are mixed together, yielding a solid insoluble substance is called precipitation reaction.** In this section we will show how to predict whether a precipitate will form when two solutions are mixed. We will use the term ion product (Q'). It is obtained by substituting initial concentrations instead of equilibrium concentrations in the expression for K_{sp} . For example, ion product expression for solid CaF_2 is given by

$$Q' = [\text{Initial conc. of } Ca^{2+}] [\text{Initial conc. of } F^{-}]^2$$

Do You Know

Precipitates are insoluble ionic solid product of a reaction in which certain cations and anions combine in an aqueous solution.

If we add a solution containing Ca^{+2} ions to a solution containing F^- ions, precipitate may or may not form. To predict whether a precipitation will occur, we compare Q' and K_{sp} . There are two possibilities.

- If $Q' > K_{sp}$, precipitation occurs and will continue until the concentration satisfy K_{sp} .
- If $Q' < K_{sp}$, precipitation does not occur.

Example 7.10

50cm³ of 0.001M NaOH is mixed with 150cm³ of 0.01M MgCl_2 . Will $\text{Mg}(\text{OH})_2$ precipitate?

K_{sp} for $\text{Mg}(\text{OH})_2 = 2 \times 10^{-11}$

Problem Solving Strategy

- Write ion product expression for solid $\text{Mg}(\text{OH})_2$
- Find total volume of solution in dm³
- Find the molar concentration of OH^- ions of given NaOH Solution in the total volume of solution.
- Find the molar concentration of Mg^{+2} ions of given MgCl_2 solution in the total volume of solution.
- Find Q' and compare it with K_{sp} value. If $Q' > K_{sp}$ precipitation will occur. If $Q' < K_{sp}$ Precipitation will not occur.

Solution

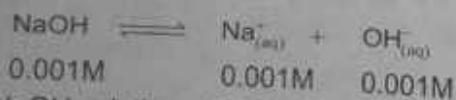
First we will determine the concentration of the ions present after mixing

Total volume of solution

$$= 50\text{cm}^3 + 150\text{cm}^3$$

$$= 200\text{cm}^3$$

$$= 0.2\text{dm}^3$$

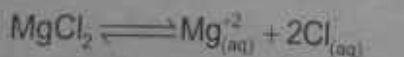


$$50\text{cm}^3 \text{ NaOH solution} = 0.05\text{dm}^3$$

$$[\text{OH}^-] = \frac{\text{Given volume}}{\text{Required volume}} \times \text{Conc.}$$

$$[\text{OH}^-] = \frac{0.05\text{dm}^3 \times 0.001\text{M}}{0.2\text{dm}^3}$$

$$= 2.5 \times 10^{-4}\text{M}$$



$$\begin{array}{ccccc} 0.01\text{M} & & 0.01\text{M} & & 2 \times 0.01\text{M} \end{array}$$

$$150\text{cm}^3 \text{ MgCl}_2 \text{ solution} = 0.15\text{dm}^3$$

$$[\text{Mg}^{+2}] = \frac{0.01\text{M} \times 0.15\text{dm}^3}{0.2\text{dm}^3}$$

$$= 7.5 \times 10^{-3}\text{M}$$

The student should be guided to choose useful information to solve various problems.

7. Chemical Kinetics

Now

$$Q' = [\text{Mg}^{+2}] [\text{OH}]^2$$

$$= (7.5 \times 10^{-3}) (2.5 \times 10^{-4})^2$$

$$= 47 \times 10^{-11}$$

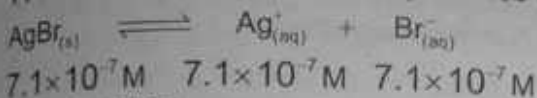
As $Q' > K_{sp}$, therefore precipitation will occur.

Example 7.11

The solubility of Ag Br is 7.1×10^{-7} M at 25°C . Calculate its K_{sp} .

Solution

7.1×10^{-7} M of dissolved Ag Br produces equal moles of Ag^+ and Br^- ions.



$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

$$K_{sp} = (7.1 \times 10^{-7}) (7.1 \times 10^{-7})$$

$$K_{sp} = 5.041 \times 10^{-13}$$



Self Check Exercise 7.12

Write K_{sp} expressions for

i. Iron(II)Hydroxide

Calcium Sulphate

ii. Lead (II) Sulphate is used as white pigment. What is the solubility of PbSO_4 ?

$$K_{sp} = 1.96 \times 10^{-8} \text{ at } 25^\circ\text{C}$$

$$(\text{Ans: } 1.4 \times 10^{-4} \text{ M})$$

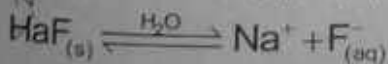
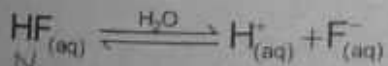
iii. Phosphate in natural water often precipitates as insoluble $\text{Ca}_3(\text{PO}_4)_2$. In Indus river concentration of Ca^{+2} and PO_4^{-3} ions is $1.0 \times 10^{-9} \text{ M}$ each. Will calcium phosphate precipitate?

$$K_{sp} = 1.2 \times 10^{-28} \text{ at } 25^\circ\text{C}$$

$$(\text{Ans: No})$$

7.5 COMMON ION EFFECT

An interesting situation arises when a weak electrolyte and a salt containing a common ion are present simultaneously in an aqueous solution. For example in a solution of weak acid, hydrofluoric acid $K_a = 7.2 \times 10^{-4}$, its salt sodium fluoride produces the common ion.



Since HF is a weak electrolyte, it slightly dissociates. NaF being strong electrolyte breaks up completely into its ions. The common ion F^- is produced by NaF will upset its equilibrium. This will increase concentration of F^- ions. According, to the Le Chatelier's principle, the equilibrium will shift to the left to use some of F^- ions. This will decrease the dissociation of HF. Thus

dissociation of HF will decrease in the presence of dissolved NaF. This means as a result of equilibrium shift, the concentration of HF will increase. See section 7.2.1 to understand the effect of change in concentration on equilibrium.

Do You Know

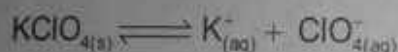
Separation and identification of cations into analytical groups is based on solubility product principle and common ion effect. In general any procedure that involves precipitation follows these principles

Similarly when a highly soluble salt is added to the saturated solution of less soluble salt containing a common ion. The degree of dissociation of less soluble salt decreases. Therefore it causes to decrease its solubility.

The term common ion effect is used to describe the behaviour of a solution in which same ion is produced by two different compounds. "The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is called common ion effect".

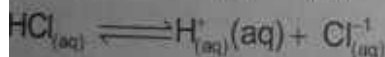
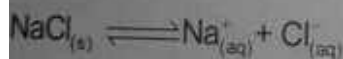
Examples 7.12

- i. Potassium perchlorate KClO_4 is moderately soluble in water. When highly soluble KCl is added to the saturated solution of KClO_4 . It causes to increase the concentration of K^+ ion.



According to the Le Chatelier's principle K^+ ions will react with ClO_4^- ions to form $\text{KClO}_{4(s)}$. This will suppress, the ionization of KClO_4 . Thus it will precipitate out.

- ii. When HCl gas is passed through the saturated solution of NaCl (Brine), it causes to increase the concentration of Cl^- ion.

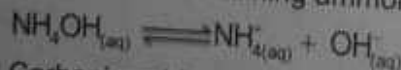


According to Le Chatelier's principle Cl^- ions will combine with Na^+ ions to form precipitate of pure NaCl .

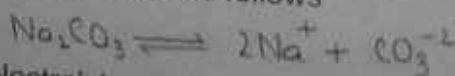
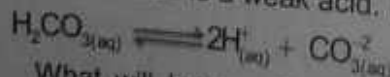


Self Check Exercise 7.12

- i. Ammonium Chloride, NH_4Cl is a water soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide.



- ii. Carbonic acid is a weak acid. It ionizes in water as follows



What will happen if a strong electrolyte such as Na_2CO_3 is added to a solution containing carbonic acid.

Key Points

- Chemical Equilibrium is a dynamic state in which the reaction proceeds with equal rates in both the directions.
- At equilibrium state reactants are converted continuously into products and vice versa, as molecules collide with each other.
- The law of mass action is a general description of the equilibrium condition. It states that for the reaction of type



The equilibrium equation is given by

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where K_c is equilibrium constant

- The equilibrium can be expressed in terms of the equilibrium partial pressure of gases as K_p .
- The reaction quotient Q has the same form as the equilibrium constant expression, but it applies to the reaction that may not be at equilibrium. If $Q > K_c$, the reaction will proceed from right to left to achieve equilibrium. If $Q < K_c$, the reaction will proceed from left to right to achieve equilibrium. If $Q = K_c$, the reaction is at equilibrium.
- There is only value of K_c for each reaction at a given temperature. However, there are infinite numbers of equilibrium positions. An equilibrium position is defined as a particular set of equilibrium concentration that satisfies the equilibrium expressions.
- The concentration of pure solids, pure liquids and solvents are constant and do not appear in equilibrium constant expression of a reaction.
- Le Chatelier's Principle allows us to predict the effect of changes in concentration, pressure and temperature on a system at equilibrium. It states that when a change is imposed on a system equilibrium, the equilibrium position will shift in a direction that tends to undo the effect of imposed change.
- Only a change in temperature changes the value of K_c for a particular reaction.
- The addition of catalyst has no effect on the equilibrium concentration of reactants and products. However, it decreases time to achieve equilibrium state.
- The principle of equilibrium can also be applied when an excess of solid is added to form a saturated solution.

References for Further Information

- Advanced Chemistry, Philip Matthews
- Fundamental's of Chemistry, David E. Guldberg
- Raymond Chang, Essential Chemistry



Exercise

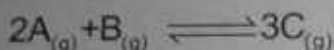
1. CHOOSE THE CORRECT ANSWER

- (i) K_c is independent of
 (a) Temperature (b) Pressure
 (c) Both temperature and pressure (d) K_p

- (ii) For which of the following reactions, K_c has units of concentration.



- (iii) For the following reaction



We can write

- (a) $K_c > K_p$ (b) $K_c < K_p$
 (c) $K_p - K_c = 0$ (d) $K_p - K_c = -1$

- (iv) When a catalyst is added to an equilibrium mixture, it decreases

- (a) Reverse reaction (b) Forward reaction
 (c) Concentrations of reaction mixture
 (d) Enthalpy of reaction (e) It has not effect

- (v) If $K_{sp} = [M^{+2}]^3 [X^{-3}]^2$, the chemical formula of compound is

- (a) MX_2 (b) M_2X_3 (c) M_3X_2 (d) M_2X_2 (e) None of these

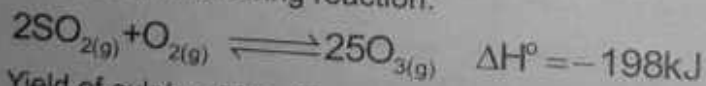
- (vi) NaCl can be purified by passing HCl gas through the _____ solution of NaCl

- (a) Dilute (b) Concentrated (c) Hot (d) Cold

- (vii) $K_c = K_p$ when Δn is equal to

- (a) Zero (b) +1 (c) -1 (d) -2

- (viii) Consider the following reaction:



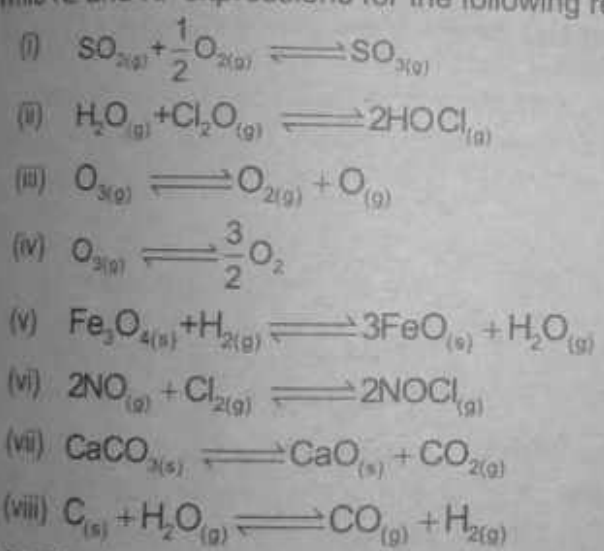
Yield of sulphur trioxide can be increased by

- a) increasing pressure
 b) increasing temperature
 c) adding catalyst
 d) increasing concentration of oxygen

1. a, b
 2. a, b, c
 3. a, b, c, d
 4. a, d

2. Define chemical equilibrium

3. State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
4. Describe the microscopic events that occur when a chemical system is in equilibrium.
5. Define and explain the following terms
 - (i) Reaction quotient
 - (ii) Solubility product
 - (iii) Common ion effect
 - (iv) Heterogenous equilibria
 - (v) Ion product
6. Explain industrial application of Le Chatelier's principle using Haber's process as an example.
7. Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.
8. 50 cm³ of acetic acid ($d = 1.049 \text{ g cm}^{-3}$) is mixed with 50 cm³ of ethanol ($d = 0.789 \text{ g cm}^{-3}$) what is the equilibrium composition of the mixture at 25°C ($K_c = 4$).
 (Ans: $\text{CH}_3\text{COOH} = 17.80 \text{ g}$, $\text{C}_2\text{H}_5\text{OH} = 12.88 \text{ g}$, $\text{CH}_3\text{COOC}_2\text{H}_5 = 50.812 \text{ g}$, $\text{H}_2\text{O} = 10 \text{ g}$)
9. Write K_c and K_p expressions for the following reactions



At a particular temperature $K_p = 0.133 \text{ atm}$. Which of the following conditions corresponds to equilibrium position for the reaction.

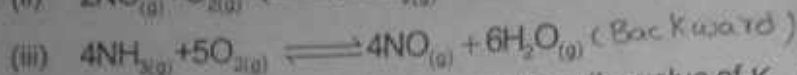
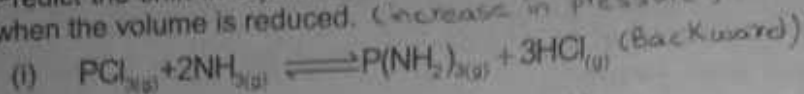
- $$\text{A}_{(g)} \rightleftharpoons 2\text{B}_{(g)}$$
- (a) $P_B = 0.175 \text{ atm}$, $P_A = 0.102 \text{ atm}$
 - (b) $P_B = 0.064 \text{ atm}$, $P_A = 0.0308 \text{ atm}$
 - (c) $P_B = 0.144 \text{ atm}$, $P_A = 0.156 \text{ atm}$

(Ans: b and c)

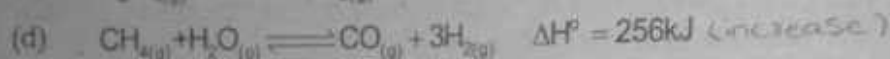
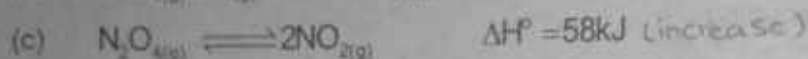
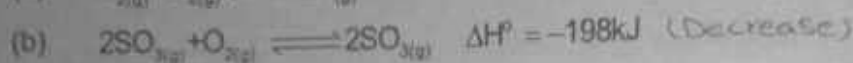
Write the expression for K_c and K_p for the following processes.

- (a) Blue vitriol is deep blue solid copper (II) sulphate pentahydrate is heated to drive off water vapours to form white solid copper (II) sulphate.
- (b) The decomposition of solid phosphorus pentachloride to gaseous phosphorus trichloride and chlorine gas

12. Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced. (increase in pressure)



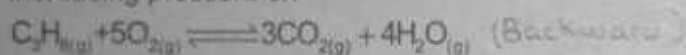
13. For each of the following reactions, predict how the value of K_c changes as the temperature is increased.



14. What is the difference between an equilibrium with a K_c value larger than one compared with an equilibrium that has a K_c smaller than one.

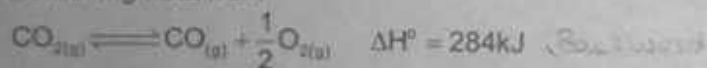
15. Describe the behaviour of the following equilibria with the stated changes

(a) Increasing pressure on

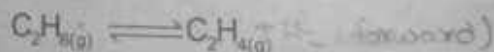


(b) Adding $\text{I}_2(g)$ to $2\text{HI}(g) \rightleftharpoons \text{I}_2(g) + \text{H}_2(g)$ (Backward)

(c) Removing heat from



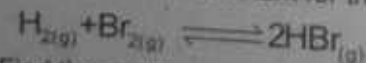
(d) Decreasing pressure on



16. A solution is prepared by mixing 50 cm^3 of $5 \times 10^{-3}\text{M}$ NaCl with 50 cm^3 of $2 \times 10^{-2}\text{M}$ $\text{Pb}(\text{NO}_3)_2$. Will a precipitate of PbCl_2 form? K_{sp} for PbCl_2 is 1.7×10^{-5} . (Ans: No)

17. When solid PbCl_2 is added to pure water at 25°C , the salt dissolves until the concentration of Pb^{2+} reaches $1.6 \times 10^{-2}\text{M}$. After this concentration is reached, excess solid remains undissolved. What is K_{sp} for this salt. (Ans: 1.6384×10^{-4})

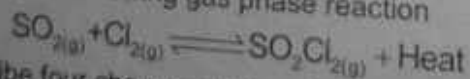
18. The equilibrium constant for the following reaction is 1.6×10^5 at 1000K



Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K .

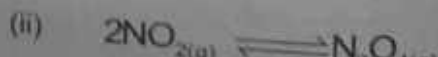
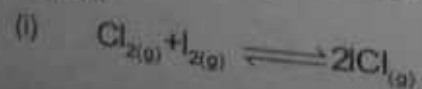
(Ans: $\text{H}_2 = \text{Br}_2 = 0.0249\text{ atm}$, $\text{HBr} = 9.95\text{ atm}$)

19. Consider the following gas phase reaction



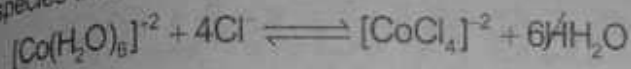
Describe four changes that would derive the equilibrium to left.

20. How would you change the volume of the following reactions to increase the yield of products.



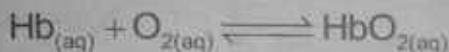
Think-Tank

22. A figurine device used to predict weather condition is blue on dry, sunny days and pink on damp, rainy days. These figurines are coated with substances containing chemical species that undergo following equilibrium.



- Identify the blue substance $[\text{CoCl}_4]^{2-}$
- Identify the pink substance $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
- How is Le Chatelier's Principle applied here.

23. The combination of oxygen with hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction. For our purpose it can be represented by the simplified equation.



where HbO_2 is oxyhaemoglobin that actually transport oxygen to tissues. The equilibrium

constant expression is $K_c = \frac{[\text{HbO}_2]}{[\text{Hb}][\text{O}_2]}$

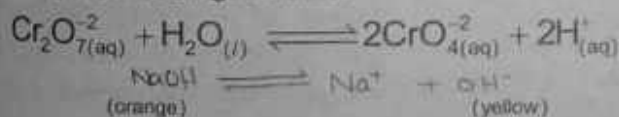
Scaling a 3km mountain can cause headache, nausea, extreme fatigue and other discomforts. Give possible explanation for it.

24. Baking Soda undergoes thermal decomposition as follows



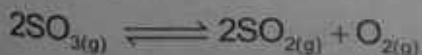
Would we obtain more CO_2 by adding extra baking soda to the reaction mixture in (a) a closed vessel (b) an open vessel.

25. Potassium dichromate solution has beautiful clear orange colour. This is due to the colour of dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$. When a salt is dissolved in water, the following equilibrium is setup, on heating solution.



What will happen if:

- dilute Sodium hydroxide is added to this solution. *Forward (Removal of Product)*
 - this is followed by dilute hydrochloric acid addition. *backward (common ion effect)*
26. If 0.350 moles of SO_3 is placed in a 1.00 dm^3 flask and allowed to come to equilibrium at a high temperature, 0.207 mole of SO_3 remains. Calculate K_c for the reaction. (Ans: 0.034)



27. For the reaction between hydrogen and iodine to form hydrogen iodide, the value of K_c is 794 at 298K but 54 at 700K what can you deduce from this information?





ACIDS, BASES AND SALTS



This is a 8 days unit

After completing this lesson, you will be able to:

- Define Bronsted and Lowery concepts for acids and bases.
- Define salts, conjugate acids and conjugate bases.
- Make a buffered solution and explain how such a solution maintains a constant pH, even with the addition of small amounts of strong acid or strong base.
- Use concept of hydrolysis to explain why the solution of a salt is not necessarily neutral.
- Define and explain leveling effect.
- Explain ionization constant of water and calculate pH and pOH in aqueous medium using given K_w values.
- Use the extent of ionization and the acid dissociation constant, K_a , to distinguish between strong and weak acids.
- Use the extent of ionization and the base dissociation constant, K_b , to distinguish between strong and weak bases.
- Define a buffer, and show with equations how a buffer system works.
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic.
- Identify conjugate acid-base pairs of Bronsted-Lowery acid and base.



Reading

INTRODUCTION

Acids were first recognized as substances that taste sour. Vinegar tastes sour because it is a dilute solution of acetic acid. Citric acid is responsible for the sour taste of a lemon. Bases, sometimes called alkalies are characterized by their bitter taste and slippery feel. Commercial preparations for unclogging drains are highly basic. A salt is an ionic substance that results from the neutralization of an acid and a base. Acid-base chemistry is important in a wide variety of everyday applications. The influence of acids on living things has assumed special importance in recent years due to the phenomenon of acid rain.

The acids classified into (i) Mineral acids or (ii) organic acids. The organic acids are much weaker than mineral acids. The organic acids are mostly found in vegetables, fruit and other stuffs. Some common organic acids and their appearance in different categories are as follows:

Organic acids	Where it is found
Lactic acid	Sour Milk
Citric acid	Citrus fruits like lemons, oranges
Formic acid	Insect bites
Tartaric acid	Grape juice
Maleic acid	Apples and

The presence of water is essential for the formation of H^+ , for example HCl is covalent in nature and does not form H^+ ions. However it forms H_3O^+ ions in the presence of H_2O .



Bases form a class of chemical substances including metal oxides and hydroxides. A soluble base is called an alkali and forms OH^- ions when dissolved in H_2O . In general the bases on hydrolysis produce alkali.



Here CaO is basic in nature where as $Ca(OH)_2$ is an alkali and a base.

A salt may be formed by the neutralisation of an acid and a base. A salt may be neutral, acidic or basic.

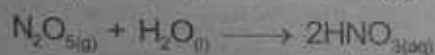
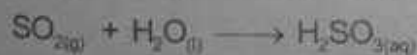
Alkalies are important in soap and detergent manufacture. Caustic soda (NaOH) is used for this purpose.

8.1 ACIDIC, BASIC AND AMPHOTERIC SUBSTANCES

The characteristics of acids and bases are well known e.g. acids turn blue litmus red and react with carbonates to evolve carbon dioxide and bases turn red litmus blue. Hydrochloric acid and nitric acid are common examples of acids, and sodium hydroxide and potassium hydroxide are common examples of bases. However, there are certain substances which are not acids or bases themselves but show acidic or basic nature when dissolved in water. For example, there are certain oxides of metals, like sodium oxide (Na_2O) and calcium oxide (CaO) which react with water to furnish bases sodium hydroxide (NaOH) and calcium hydroxide [$Ca(OH)_2$].



Thus, these oxides are basic in nature. On the other hand certain non-metal oxides like carbon dioxide (CO_2) sulphur dioxide (SO_2) and nitrogen pentoxide (N_2O_5) when react with water yield carbonic acid (H_2CO_3) sulphurous acid (H_2SO_3) and nitric acid (HNO_3). Such oxides are thus acidic in nature.



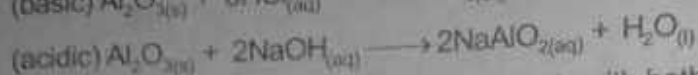
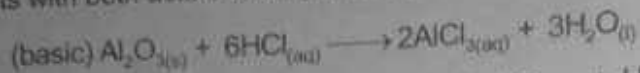
Do You Know

Oxides release a gas which turns into sulphuric acid when it reaches your eyes, making them burn.

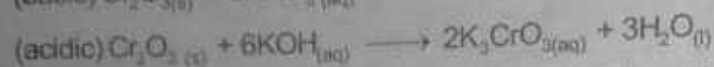
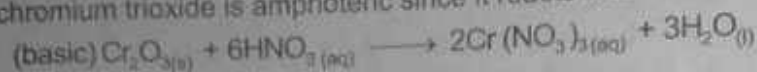
Do You Know

Lemon juice contains citric and ascorbic acid.

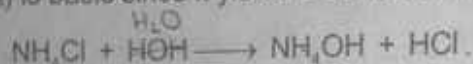
Certain oxides are on the border line of being acidic or basic. These oxides which tend to be insoluble in water, are soluble in both acids and bases. They are said to be amphoteric in character that is both acidic and basic. For example aluminium oxide (Al_2O_3) is amphoteric and reacts with both acidic and basic solutions:



Also, chromium trioxide is amphoteric since it reacts with both acids and bases.



In addition to oxides, certain salts are also acidic and basic in nature e.g. ammonium chloride (NH_4Cl) is acidic because when dissolved in water it furnishes an acidic solution. potassium carbonate (K_2CO_3) is basic since it yields a basic solution in water.



8.2 BRONSTED LOWERY CONCEPTS FOR ACIDS AND BASES:

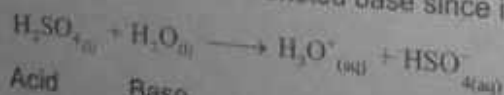
The concept of acids and bases was further elaborated by J. Bronsted and T. Lowry independently, by defining them in a different manner. According to these definitions, a Bronsted acid is a proton donor and Bronsted base is a proton acceptor. In this respect, a proton is defined as the nucleus of a hydrogen atom (H^+) and it has nothing to do with the protons in a carbon atom, or a sodium atom or any other atom. Hydrochloric acid is a Bronsted acid since it donates a proton to water according to the following equation.



Acid Base

Since water accepts a proton, it is a Bronsted base. After accepting a proton, water is converted to hydroxonium ion (H_3O^+). The hydroxonium ion is infact a hydrated proton. Some more common Bronsted acids are sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) etc.

The Bronsted bases have been defined as those species which accept a proton. Thus, in the following equation, water is a Bronsted base since it accepts a proton from sulphuric acid.



Acid Base

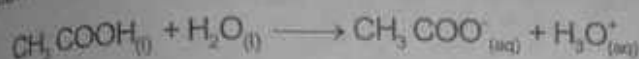
Also, in the equation below, ammonia accepts a proton from water. Therefore, ammonia is a Bronsted base and water is a Bronsted acid here:





Base Acid

It is important to note that water behaves as a Bronsted acid in presence of ammonia and as a Bronsted base in presence of hydrochloric acid or sulphuric acid. There are many other examples of this type of behaviour. For example, in the equations given below acetic acid is Bronsted acid or a Bronsted base in the second equation.



Acid Base



Base Acid

Interesting Information

The wild lupin plant takes nitrogen from the atmosphere and produces ammonia. It was that ammonia to fertilize the soil for itself and surrounding plants.

8.2.1 Salt, Conjugated Acids and Conjugated Bases

Salts: The joint substance obtained as a result of neutralization of acids and bases are called salts.



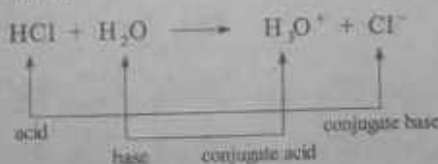
which substance is a salt in this reaction

Conjugate acids and conjugate bases:

Conjugate acid is a species which is formed as a result of acceptance of proton by a base. Every Bronsted acid has a conjugate base.

Conjugate base is a species which is left behind after donation of a proton from the acid.

e.g. Ionisation of HCl in water

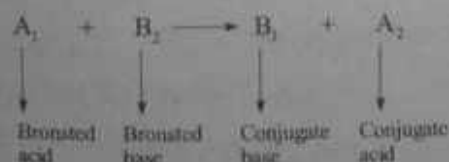


Do You Know

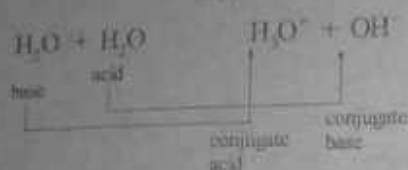
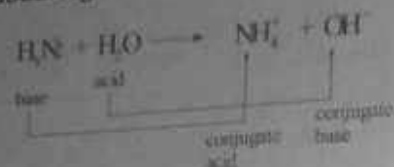
A strong acid produces a relatively weak conjugate base. Likewise a strong base produces a relatively weak conjugate acid.

8.3 CONJUGATE ACID – BASE PAIRS

In an acid-base reaction, an acid yields a base (conjugate) and base after accepting proton yields a conjugate acid. The acid-base reaction is represented as



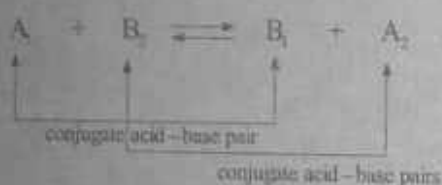
The conjugate acid-base pairs are species on opposite sides of an equation that differ by a proton. The weaker acids have strong conjugate base pairs and stronger acids have weaker conjugate bases e.g.



The water is amphoteric in nature i.e. it is acidic as well as basic in nature.

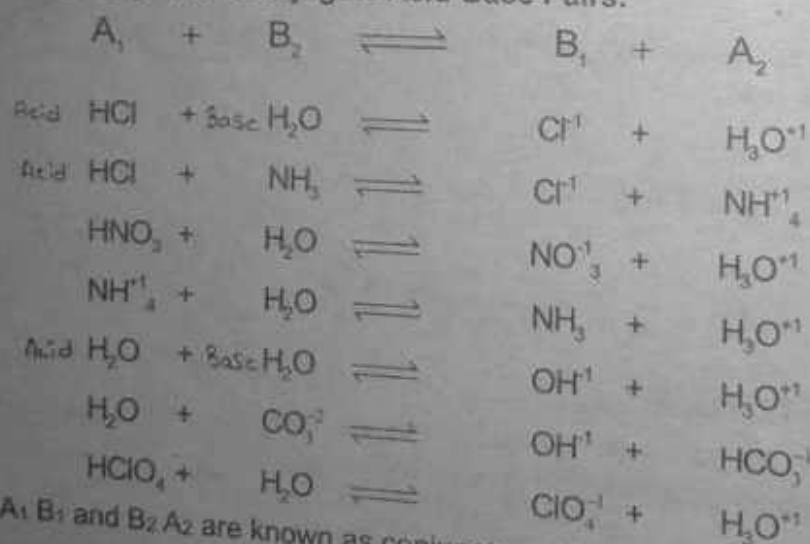
8.3.1 Identification of Conjugate Acid-Base Pairs

The general notation of conjugate acid-base pair is



Each acid has a conjugate base and each base has a conjugate acid.

Particular Examples of Conjugate Acid-Base Pairs:



A₁ B₁ and B₂ A₂ are known as conjugate acid-base pairs.

8.4 STRENGTH OF ACIDS AND BASES:

Different Bronsted acids donate proton to different extents. An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid. For example, hydrochloric acid is a relatively stronger acid than acetic acid. Also, acetic acid is relatively stronger than water. The ability of an acid to donate proton is called 'strength of acid' or the 'acid strength'. Similarly, the bases also differ in their ability to accept proton. A base which can accept proton to higher degree than another base is a relatively stronger base. Thus ammonia is a relatively stronger base than water because ammonia can accept a proton to a higher degree than water.

8.4.1 Ionisation constant of Water and Calculation of pH and pOH in Aqueous Medium using Given K_w Values

Water is a unique compound due to its ability to accept or donate proton under different environments. It has been mentioned earlier that water acts as a Bronsted acid in presence of ammonia, and as a Bronsted base in presence of hydrochloric acid. In fact, Water itself undergoes ionization to a small extent as shown in the following equation:



This reaction is regarded as auto ionization of water. Here, a molecule of water (which is acting as an acid) donates a proton to another molecule of water (which is acting as a-base) and two species, a hydronium ion and a hydroxide ion, are formed. In this equation, there are two acid-base conjugate pairs; the first one is water-hydroxide ion (acid-conjugate base) and the second water hydronium ion (base conjugate acid). In fact, there is an equilibrium between water molecules (on the left side of the equation) and the hydronium ions and hydroxide ions on the right side of the equation). The equilibrium constant (K) for this equilibrium can be expressed by the following equation.

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

In this equation $[\text{H}_3\text{O}^+][\text{OH}^-]$ and $[\text{H}_2\text{O}]$ are the concentration of hydronium ion, hydroxide ion and water at equilibrium stage. Since water is a solvent, the concentration of water, $[\text{H}_2\text{O}]$ is in large excess, therefore it remains constant. The above equation may be re-written as:

$$K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

the term $K[\text{H}_2\text{O}]^2$ is the product of two constants, and is

$$K[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \therefore \text{H}_2\text{O}^+ = \text{H}^+$$

K_w is termed as the ion-product constant of water. Since $[\text{H}_3\text{O}^+]$ is the concentration of hydrated protons at equilibrium, the above equation corresponds to:

The Student must be guided to use this information in various ways:

$$K_w = [H^+][OH^-]$$

In pure water at 25°C, the concentration of H^+ and OH^- are equal and found to be 1.0×10^{-7} M each. Thus:

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

It has been noted that whether in pure water or in a solution of dissolved species, the following relationship always holds.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Whenever $[H^+] = [OH^-]$, the aqueous solution is found to be neutral, neither acidic nor basic.

$$[H^+] > [OH^-] \quad \text{Acidic solution}$$

$$[OH^-] > [H^+] \quad \text{Basic solution}$$

It is to be noted that, because K_w is an equilibrium constant, it is temperature dependent; thus, at 40 °C $K_w = 3.8 \times 10^{-14}$ which corresponds to

$$[H^+] = 1.9 \times 10^{-7} \text{ M and } [OH^-] = 1.9 \times 10^{-7} \text{ M as } [H^+] = [OH^-]$$

Since the concentration of $[H^+]$ and $[OH^-]$ are usually very small numbers and inconvenient to work with, a more practical measure called pH was proposed and defined as:

$$pH = -\log [H^+]$$

It means that pH of a solution is given by the negative logarithm of the $[H^+]$ concentration (in mol/dm³). However it must be kept in mind that pH being a logarithmic value, does not have any units, the pH concept implies that at 25°C, the different types of solutions will show the following behaviours:

$$\text{Acid solution: } [H^+] > 1.0 \times 10^{-7} \text{ M, pH} < 7.00$$

$$\text{Basic solution: } [H^+] < 1.0 \times 10^{-7} \text{ M, pH} > 7.00$$

$$\text{Neutral solution: } [H^+] = 1.0 \times 10^{-7} \text{ M, pH} = 7.00$$

A scale analogous to the pH can be devised using the negative logarithm of the H^+ concentration.

Example 8.1:

The concentration of $[OH^-]$ ion in a household ammonia solution is 0.005M. Calculate the concentration of $[H^+]$ in it.

Solution:

$$[OH^-] = 0.005 \text{ M}$$

$$K_w = [H^+][OH^-]$$

$$1.0 \times 10^{-14} = [H^+] \times 0.005$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.005} = 2.0 \times 10^{-12} \text{ M}$$

$$\begin{aligned} \text{As } K_w &= [\text{H}^+][\text{OH}^-] \\ 1.0 \times 10^{-14} &= [\text{H}^+][\text{OH}^-] \end{aligned}$$

Taking log of both sides

$$\begin{aligned} \log(1.0 \times 10^{-14}) &= \log[\text{H}^+] + \log[\text{OH}^-] \\ -14 &= -\log[\text{H}^+] - \log[\text{OH}^-] \\ 14 &= (-\log[\text{H}^+]) + (-\log[\text{OH}^-]) \\ 14 &= \text{pH} + \text{pOH} \end{aligned}$$

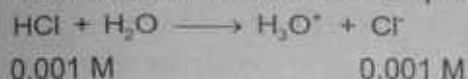
This equation provides another way to express the relationship between the $[\text{H}^+]$ and $[\text{OH}^-]$ concentrations.

Example 8.2:

Calculate the pH of 0.001 M aqueous hydrochloric acid solution.

Solution:

Hydrochloric acid ionises in water completely therefore,



$[\text{H}_3\text{O}^+]$ is in fact the same as $[\text{H}^+]$

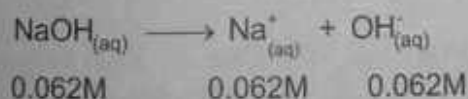
Therefore $[\text{H}^+] = 0.001 \text{ M}$

$$\begin{aligned} \text{pH} &= -\log(0.001) \\ &= -\log 10^{-3} \\ &= 3.00 \end{aligned}$$

Therefore, the pH of 0.001 M aqueous hydrochloric acid is 3.00

Example 8.3:

Calculate the pH of 0.062 M NaOH solution.

Solution:

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] \\ &= -\log[0.062] \\ &= 1.21 \end{aligned}$$

$$\begin{aligned} \text{Now } \text{pH} + \text{pOH} &= 14 \\ \text{pH} &= 14 - \text{pOH} \\ &= 14 - 1.21 \\ &= 12.79 \end{aligned}$$

Self Check Exercise 8.1

What is the pH of a solution containing 1.95g pure H_2SO_4 per dm^3 of solution? (Ans: pH = 1.4)

TITRATION:

"It is defined as a method to find the volume of the standard solution required to react completely with known volume of another solution under analysis".

8. Acid, Bases and Salts

Acid-base titrations are conducted using burettes and volumetric pipettes. Generally acid solution is placed with the burette. A fixed volume of base is placed into a conical flask along with a few drops of the appropriate acid-base indicator. Acid from the burette is added to the base until the indicator changes colour. This change of colour indicates the end point of titration. In the neutralization of a strong acid with a strong base, phenolphthalein is used as an indicator. It imparts pink colour to the base solution. At the end point, solution just becomes colourless. The molarity of the acid solution under test is determined with the help of the following equation.

$$M_1 V_1 = M_2 V_2$$

Where M_1 = Molarity of the base
 V_1 = Volume of the base taken in flask
 M_2 = Molarity of the acid
 V_2 = Volume of acid used from the burette

Knowing the three parameters, the fourth can be calculated.



Activity 1

Activity for Students

Perform acid-base titrations to calculate molarity and strength of given sample solutions.

Suppose we take strong acid (HCl) and strong base (NaOH) solutions. Molarity of NaOH is known and that of HCl is to be determined. For titration purposes phenolphthalein is used as an indicator. HCl is taken in the burette while 10 ml of NaOH in the conical flask. Add few drops of phenolphthalein in NaOH solution from the Conical flask in it drop by drop till the pink color just disappears. The disappearance of pink colour gives the end point.

According to molarity concept

$$M_1 V_1 = M_2 V_2$$



$$M_1 \times 10 = \frac{1}{10} \times 10 \quad \text{or} \quad M_1 = \frac{1}{10} = 0.1\text{M}$$

Thus molality of the given solution is 0.1M.

Strength dm^3 = molality $\times$ molar mass

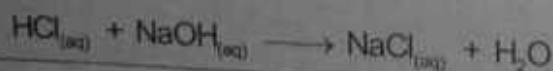
$$= \frac{1}{10} \times 36.5 = 3.65\text{g dm}^{-3}$$

Self Check Exercise 8.2

Example 5:

In a titration it is found that 25 cm^3 of 0.12M NaOH is neutralized with 30 cm^3 of HCl of unknown concentration. Calculate concentration and strength of HCl solution.

Solution:



The Student should be guided to repeat this information in...

8. Acid, Bases and Salts

205

$$n_1 = 1 \quad n_2 = 1$$



$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 30}{1} = \frac{0.12 \times 25}{1}$$

$$M_1 = 0.1\text{M}$$

Thus Molarity of HCl solution is 0.1M.

$$\text{Strength of solution} = \text{Molarity} \times \text{Molar mass}$$

$$\text{Strength of HCl solution} = 0.1 \times 36.5$$

$$= 3.65\text{g dm}^3$$

8.4.2 Strong and Weak Acids

The extent of ionization and the acid dissociation constant K_a can be used to distinguish between strong and weak acids.

According to the Bronsted-Lowry definition an acid is a proton donor species. Different acids have a tendency to donate proton but this tendency is different. An acid may donate proton to very high degree, a high degree or to small degree or very small degree. Depending on this ability of donation of proton, an acid is regarded as strong acid or a weak acid. Strong acids donate proton to a greater degree than the weak acids. The strength of an acid is generally expressed in terms of the acid ionization constant, K_a . Consider the case of ionization of a general acid HX in water. In this aqueous solution, the established equilibrium may be represented as follows:



The equilibrium constant K for this ionisation process may be written as follows:

$$K = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}][\text{H}_2\text{O}]}$$

$$\text{or } K [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, $K [\text{H}_2\text{O}]$ is another constant and is designated as K_a thus,

$$K [\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]}$$

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state. It must be kept in mind that the acid dissociation constant, K_a , is dependent on temperature. Therefore, the value of K_a should be mentioned along with the temperature at which K_a was determined. Dissociation constant, K_a , of

acetic acid in water at 25°C is 1.8×10^{-5} . The comparison of K_a values of different acids provides a method to compare their strengths.

"The greater the value of K_a , the stronger is the acid".

The value of K_a are usually inconvenient numbers, therefore, for convenience these values are converted to pK_a values. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Since pK_a refers to the negative logarithm of K_a , smaller the value pK_a stronger shall be the acid because smaller pK_a value corresponds to a greater K_a value. In table 8.2 are listed the ionisation constants and pK_a values of some common acids in water at 25°C. Which acid is strongest acid? Which acid is weakest acid?

Table 8.2: Ionisation constants and pK_a of Acids

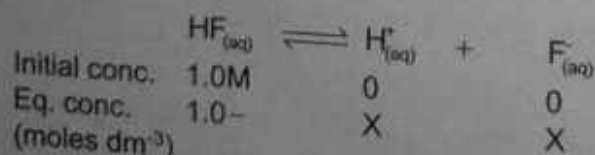
Name of Acid	Formula	K_a	pK_a
Perchloric acid	HClO_4	1.0×10^{10}	-10.0
Hydroiodic acid	HI	1.0×10^{10}	-10.0
Hydrobromic acid	HBr	1.0×10^9	-9.0
Hydrochloric acid	HCl	1.0×10^6	-6.0
Sulphuric acid	H_2SO_4	1.0×10^3	-3.0
Hydrofluoric acid	HF	1.0×10^{-4}	+3.1
Formic acid	HCOOH	1.0×10^{-4}	+3.7
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	6.3×10^{-5}	+4.2
Acetic acid	CH_3COOH	1.8×10^{-5}	+4.7
Phenol	$\text{C}_6\text{H}_5\text{OH}$	1.3×10^{-10}	+8.9
Water	H_2O	1.8×10^{-16}	+15.7

Which acid is stronger HCl or HF ?

Example 6:

Calculate concentration of H^+ ions of a solution that contains 1.0M HF ($K_a = 7.2 \times 10^{-4}$)

Solution:



The Student should be guided to distinguish...

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$7.2 \times 10^{-4} = \frac{x \cdot x}{1.0 - x}$$

Since x is very small as compared to 1.0, the term in the denominator can be approximated as follows:

$$1.0 - x = 1.0$$

$$7.2 \times 10^{-4} = \frac{x^2}{1}$$

$$x = 0.268M$$

$$[H^+] = 0.268M$$

Example 8.7:

The pH of a 0.1M solution of an acid is 2.85. Calculate the ionization constant, K_a of the acid.

Solution:

Using the pH value, the equilibrium concentration of the acid and the conjugate base can be calculated. These concentrations may then be used to calculate K_a .

$$pH = -\log [H^+]$$

$$2.85 = -\log [H^+]$$

Taking antilog "of" both side $[H^+]$ turns out to be $1.4 \times 10^{-3}M$.

Now equilibrium is considered:

	Acid _(aq)	H^+ _(aq)	conjugate base _(aq)
Before equilibrium	0.100M	0.000	0.000
Change	0.0014M	0.0014M	0.0014M
At equilibrium	0.0986M	0.0014M	0.0014M

$$K_a = \frac{[H^+][\text{conjugate base}]}{[\text{acid}]}$$

$$= \frac{(0.0014)(0.0014)}{0.0986}$$

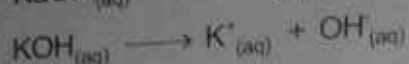
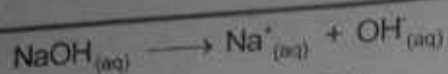
$$= 1.99 \times 10^{-5}$$

Thus the ionisation constant, K_a is 1.99×10^{-5}

8.4.3 Strong and Weak Bases

Use the extent of ionization and the base dissociation constant K_b to distinguish between strong and weak bases.

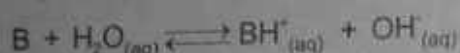
The strength of a base is the ability to accept a proton from a solvent. Hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide are strong bases and ionize completely in aqueous solution.



The OH^- ion thus formed is a Bronsted base because it can accept proton H^+ .



The ability of a base to accept a proton from an acid, usually water, is termed as strength of the base. For a base B, an equilibrium reaction with water can be represented by the following equation:



The equilibrium constant K_b is referred to base ionization constant and can be derived in the same way as K_a for acids. Thus:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

K_b value will be large if degree of ionization of the base B is high i.e. if the base B is strong. The Value of K_b will be small for a weak base B. Again, for convenience, a parameter $\text{p}K_b$ has been devised to express K_b value in convenient numbers. Thus, $\text{p}K_b$ is defined as the negative logarithm of K_b .

$$\text{p}K_b = -\log K_b$$

Table 8.3: K_b and $\text{p}K_b$ Values of Some Common Bases

Name of Base	Formula	K_b	$\text{p}K_b$
Diethylamine	$(\text{C}_2\text{H}_5)_2\text{NH}$	9.6×10^{-4}	3.02
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	5.6×10^{-4}	3.25
Methylamine	CH_3NH_2	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	$\text{C}_5\text{H}_5\text{N}$	5.6×10^{-9}	8.25
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	4.3×10^{-10}	9.37

According to these values ammonia is a stronger base than pyridine and aniline but weaker than methylamine and ethylamine. Also, diethyl amine is a strongest base among all those listed in the table.

4.4 Relationship of K_a and K_b :

For a conjugate acid base pair an important relationship exists between K_a , the acid dissociation constant, and K_b , the base dissociation constant. This is given by,

$$K_a \times K_b = K_w$$

The student should be guided to distinguish between weak and strong bases.

This relationship can be proved by considering the ionization of an acid HA and writing equation for its K_a .



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The equilibrium for the conjugate base is



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Multiplying the expression for K_a and K_b .

$$K_a K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$\text{Thus } K_a K_b = [\text{H}^+][\text{OH}^-] = K_w$$

This result leads to an important conclusion that if the value of K_a is known K_b can be calculated since $K_a K_b = K_w$.

$$\log(K_a K_b) = \log K_w$$

$$\log K_a + \log K_b = \log K_w$$

On changing the signs from plus to minus in the above equation.

$$(-\log K_a) + (-\log K_b) = (-\log K_w)$$

Note that in terms of $\text{p}K_a$ & $\text{p}K_b$ the equation becomes

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

$$\text{As } \text{p}K_w = 14 \text{ at } 25^\circ\text{C}$$

$$\text{p}K_a + \text{p}K_b = 14 \text{ at } 25^\circ\text{C}$$

Example 8.8 (a)

The $\text{p}K_a$ of acetic acid at 25°C is + 4.76. Calculate the $\text{p}K_b$ of the conjugate base of acetic acid.

Solution:

$$\text{p}K_a + \text{p}K_b = 14.00$$

$\text{p}K_a$ of acetic acid is given as + 4.76

$$4.76 + \text{p}K_b = 14 \quad \text{or} \quad \text{p}K_b = 9.24$$

Example 8.8 (b)

The $\text{p}K_b$ of pyridine at 25°C is 8.25. Calculate the $\text{p}K_a$ of the

Solution:

$$pK_a + pK_b = 14.00$$

$$pK_b \text{ of pyridine} = + 8.25$$

$$\text{therefore } pK_a + 8.25 = + 14.00$$

$$\text{and } pK_a = + 14.00 - 8.25$$

$$= + 5.75$$

Therefore, the pK_a of the conjugate acid of pyridine turns out to be +5.75 one of the important conclusion of the equation $K_a K_b = K_w$ is

$$K_a = \frac{K_w}{K_b}$$

$$\text{and } K_b = \frac{K_w}{K_a}$$

Since K_w is constant at a given temperature, it may be deduced that K_a is inversely proportional to K_b . Thus, stronger the acid, weaker is its conjugate base. It can also be seen that stronger a base, weaker is its conjugate acid. For example, ammonia is a weaker base ($pK_b = + 4.76$) than diethylamine ($pK_b = 3.02$), therefore the conjugate acid of ammonia is a stronger acid than the conjugate acid of diethylamine. Similarly, the conjugate base of a weak acid, water ($pK_a = + 6.00$) is a stronger base than the conjugate base of stronger acid hydrochloric acid ($pK_a = -7.00$). Thus, hydroxide ion (OH^-) is a stronger base than the chloride ion (Cl^-).



Self Check Exercise 8.3

Example 9:

What is the percentage ionisation of acetic acid in a solution in which 0.1 M of it has been dissolved per dm^3 of the solution

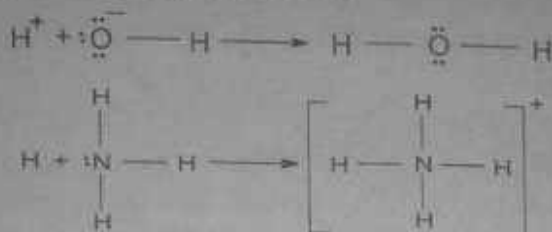
$$K_a = 1.8 \times 10^{-5}$$

$$\text{Hint: Percentage ionisation} = \frac{\text{concentration of ionised acid}}{\text{original concentration}} \times 100$$

(Ans. 1.3%)

8.5 LEWIS DEFINITIONS OF ACID AND BASE

So far, acid-base concept has been discussed in terms of the Bronsted – Lowery Theory of acids and bases. To behave as a Bronsted base, a substance must be able to accept proton, thus both the hydroxide ion and ammonia are bases:



It should be noted that the hydroxide ion and ammonia, both, have at least one unshared pair of electrons which is used to accept the proton. G.N Lewis, in 1932, put forward his acid-base theory on the basis of this electron pair. According to Lewis definition, a base is a substance that donates a pair of electrons, and an acid is a substance which can accept a pair of electrons. For example, the hydroxide ion (OH^-) is a Lewis base because it donates a pair of electron and the proton (H^+) is a Lewis acid-since it accepts a pair of electrons. The significance of the Lewis acid-base concept is that it is much more general than other concepts. It may include such acid-base reactions which are not covered by the Bronsted–Lowery theory. One such example is the reaction between ammonia and boron trifluoride (BF_3) illustrated by the following equation:



The vacant, unhybridized 2p orbital of boron atom in boron trifluoride accepts the electron pair from ammonia. Thus in this reaction ammonia is a Lewis-base and boron trifluoride is a Lewis acid although no proton transfer is observed here.

In Table 8.4 some common Lewis acids and bases are listed. A careful look at this table reveals that Lewis acids have the ability to accept electron pair whereas the Lewis bases are capable of donating electron pair.

Table 8.4: Some common Lewis Acids and Bases

Lewis Acids		Lewis Bases	
Name	Formula	Name	Formula
Proton	H^+	Hydroxide ion	OH^-
Boron trifluoride	BF_3	Ammonia	NH_3
Aluminium chloride	AlCl_3	Carbon monoxide	CO
Silver cation	Ag^+	Water	H_2O
Carbon dioxide	$\text{O}=\text{C}=\text{O}$	Cyanide ion	$\text{C}\equiv\text{N}^-$

8.6 BUFFER SOLUTIONS AND THEIR APPLICATIONS (Major Concept)

Multiple industrial processors' rely on buffers, including pharmaceuticals and to textiles.

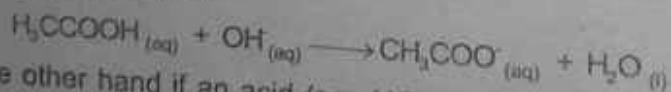
A buffer solution is a solution the pH of which does not change significantly when a small amount of acid or base is added to it. Such a solution has a constant pH which does not change on keeping it for a long time.

An aqueous solution of a weak acid or a weak base contains two substances which react with each other to a limited extent. These substances are acid and water or base and water. When a third substance is added to this solution, an effect can be produced on the original pair of reactants in solution (acid and water or base and water). The third substance may suppress the reaction of the original two reactants. For example, if sodium acetate (CH_3COONa) is added to an aqueous solution of acetic acid (CH_3COOH), it does not react directly with acetic acid or with water. However, the increase of the acetate ions suppresses the ionisation of acetic acid. The equation below illustrates the equilibrium of the aqueous acetic acid solution:

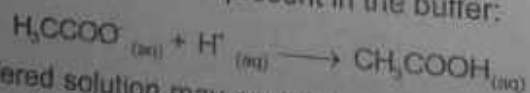


On addition of sodium acetate (CH_3COONa) the solution receives sodium ions (Na^+) and acetate ions CH_3COO^- as a result of ionisation of sodium acetate. The presence of sodium ion does not affect the equilibrium since it is not involved in this reaction. However, the increase in the concentration of acetate ions (appearing on the right side of the equilibrium equation) will shift the equilibrium to the left.

Now consider a solution containing both a weak acid and its conjugate base (as a soluble salt). Such a solution is called a buffer solution. One buffer solution can be made by dissolving sodium acetate and acetic acid in water. It may be recalled that acetic acid is a weak acid and acetate ion is a conjugate base of acetic acid. Thus in this solution both acetic acid and its conjugate base are present. The acidity of this solution is less than a solution of acetic acid because the acetate ions hinder the ionisation of acetic acid. In addition, the buffer solution has a special character of resisting change in its pH even when a small amount of strong acid or strong base is added to it. Such a solution has the ability to neutralize either added acid or base. If base is added to the buffer solution, the hydroxide ions (OH^-) will be neutralized by the acid (acetic acid) in the buffer.



On the other hand if an acid (say HCl) is added, the protons (H^+ ion) produced will be consumed by the acetate ions present in the buffer:



A buffered solution may contain a weak acid and its salt from strong base (e.g. HF and NaF) or weak base and its salt from strong acid (e.g. NH_3 and NH_4Cl). By choosing appropriate components, a solution can be buffered at a desired pH.

8. Acid, Bases and Salts

The following example explains the calculations associated with buffered solutions.

The concentration of conjugate base in the reaction mixture is predominately supplied by the salt which is a strong electrolyte. Therefore, assuming the concentration of conjugate base equal to that of salt and original concentration of acid as equilibrium concentrations, pH of a buffer can be calculated.



Science Titbits

Fermentation reactions such as in breads the pH of dough drop with the production of CO_2 and some organic acids. In this case both natural buffers milk and flour, as well as sodium hydrogen carbonate can be used to limit pH variations during fermentation.

Example 8.9:

- Calculate the pH of an acetic acid-sodium acetate buffer solution containing 1.0 moles of each component.
- What will be the pH of this solution after addition of 0.01 mole of hydrochloric acid gas to 1 dm^3 volume? Assume that the volume of solution remains unchanged on addition of hydrochloric acid. (K_a for acetic acid is 1.8×10^{-5}).
- The pH of the buffer solutions can be calculated by assuming the equilibrium concentration of both the acid and its conjugate base as starting concentration.

Thus $[\text{CH}_3\text{CO}_2\text{H}] = 1.0\text{M}$ $[\text{CH}_3\text{COO}^-] = 1.0\text{M}$

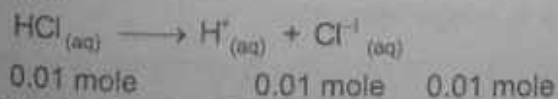
For acetic acid dissociation

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

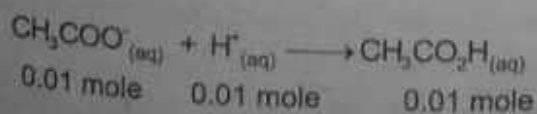
$$1.8 \times 10^{-5} = \frac{[1.0][\text{H}^+]}{[1.0]}$$

Thus, the pH of buffer solution is 4.745.

(d) After HCl addition:



Initially, there were 1.0 mole of CH_3COOH and 1.0 mole of CH_3COO^- present per dm^3 of the solution. After addition of hydrochloric acid 0.01 mole of CH_3COO^- ions are combined with the H^+ ions formed from dissociation of 0.01 mole of added hydrochloric acid. This can be written as:



Thus, the numbers of moles of acetic acid and acetate ions, after addition of hydrochloric acid are:

$$\text{CH}_3\text{CO}_2\text{H} : (1.0 + 0.01) \text{ mole} = 1.01 \text{ mole}$$

$$\text{CH}_3\text{COO}^- : (1.0 - 0.01) \text{ mole} = 0.99 \text{ mole}$$

The equilibrium equation for this new situation can be written

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

$$\text{or } [\text{H}^+] = \frac{K_a[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{1.8 \times 10^{-5} (1.01)}{0.99}$$

$$\text{pH} = -\log (2.210^{-5}) \\ = 4.736$$

Notice there is a slight change in pH from 4.745 to 4.736 that is only a difference of 0.009. Thus a buffer does a very good job in limiting the change in pH to a very small amount. Some important facts about buffer solutions are as follows:

1. Buffer solution can be prepared by combining, in aqueous solution, a weak acid and its salt with strong base or a weak base and its salt with strong acid.
2. A buffer solution resists change in its pH even if a small amount of strong acid or a base is added to it.
3. A buffer solution maintains the stability of its pH by shifting their equilibrium to consume added H^+ ion or to replace H_3O^+ ions which have reacted with the added OH^- ions.
4. An aqueous solution of a strong acid and its conjugate base (as its soluble salt) can not act as a buffer solution. Since the strong acid is completely ionized already, addition of small amount of base (OH^- ions) will consume the H_3O^+ ions which can not be replaced and the pH of the solution will change. If a small amount of strong acid is added to this solution, the equilibrium will not shift to the left because the acid already present is a strong acid. Also a solution of strong base and its conjugate acid do not form a buffer solution due to similar reasons.
5. Some common examples of buffers are acetic acid/sodium acetate buffer, phosphoric acid/potassium dihydrogen phosphate buffer and formic acid/sodium format buffer.

Applications of buffer solutions:

- (1) Buffer solutions play an important role in several industrial processes. For example they are used in the manufacture of photographic materials, leather and dyes
- (2) They are also used in the process of electroplating and analytical procedures.

8. Acid, Bases and Salts

- (3) The buffer solutions are also used for calibration of pH meters.
- (4) In nature, many biological systems depends upon buffer action to preserve a constant pH. e.g. the pH of human blood is maintained between 7.35 to 7.45. The pH of tears is also maintained at 7.40 whereas the stomach juices are known to have pH preserved at 1.65 – 1.75. Milk and egg white (protein) show their pH as 6.7 – 6.8 and 8.0 – 8.1 respectively.
- (5) Buffers are used to maintain the pH of culture media for the growth of bacteria in bacteriological applications.

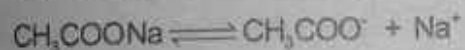
Composition of a buffer solution:

A buffer solution can be made in two ways:

- (1) By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. e.g. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.
- (2) By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with pH more than 7. e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

Buffer Action:

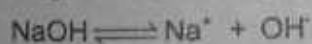
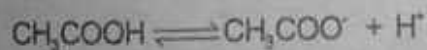
- (i) Let us take a buffer solution of CH_3COOH and CH_3COONa . Common ion effect helps us to understand how will buffer work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa , a strong electrolyte is added to CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to common ion effect of CH_3COO^- .



Suppose we add a few drops of HCl to it. Its H^+ ions are used up by CH_3COO^- .

Thus the addition of HCl will not change the pH of the buffer solution.

- (ii) In the same buffer solution, if a strong base is added it is neutralised by the acid.



Thus the addition of NaOH will not change value of pH.

Example 8.10:

What is the pH of buffer if concentration of CH_3COOH is 0.1 M and CH_3COONa is 1.0 M pK_a for CH_3COOH is 4.76?

Solution:

Concentration of CH_3COOH = 0.1 M

Concentration of CH_3COOH = 1.0 M

The formula to determine pH value is

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}](\text{i.e. } \text{CH}_3\text{COONa})}{[\text{acid}](\text{i.e. } \text{CH}_3\text{COOH})}$$

$$\text{pH} = 4.76 + \log \left(\text{since } \frac{1.0}{0.2} = \frac{10}{1} \right)$$

$$\text{pH} = 4.76 + \log 10 \quad (\text{as } \log 10 = 1)$$

$$\text{pH} = 4.76 + 1.00$$

$$\text{pH} = 5.76$$



Self Check Exercise 8.4

Calculate the pH of a buffer solution in which 0.11 Molar CH_3COONa and 0.09 Molar CH_3COOH solutions are present.

K_a for CH_3COOH is 1.8×10^{-5}

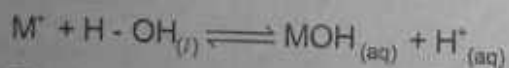
(Ans: 4.83)

8.7 SALT HYDROLYSIS

Consider the following observations:

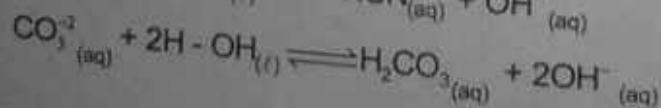
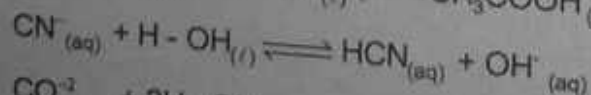
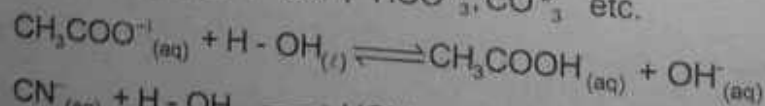
- Aqueous solution of NH_4Cl turns blue litmus red.
- Aqueous solution of K_2CO_3 turns red litmus blue.
- Aqueous solution of NaCl has no action on litmus solutions.

These observations can be explained on the basis of Bronsted-Lowry acid-base theory. When a salt (MX) is dissolved in water, it splits up into its M^+ and X^- ions. These ions may react with water and give following reactions:



Since H^+ and OH^- ions are produced in these reactions, the solution of the salt may be acidic or basic. In salts anions are derived from acids and cations from bases. The anions of weak acids are strong conjugate bases. Such anions react with water producing basic solutions.

For example: CH_3COO^- , CN^- , HCO_3^- , CO_3^{2-} etc.



The student should be quiet in class.

8. Acid, Bases and Salts

217

Anions like Cl^- , NO_3^- , SO_4^{2-} , are so weak conjugate bases that, they do not react with water. Cations of weak bases are strong conjugate acids. Such cations react with water producing acidic solutions.

For example: Cu^{2+} , Al^{3+} , NH_4^+ , etc.



Cations like

Na^+ , K^+ , Ca^{2+} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc. are so weak conjugate acids that they do not react with water.

These reactions are called hydrolysis reactions. "The reaction of cations and anions of salts with water is called hydrolysis."

Hydrolysis is different from hydration. In hydrolysis H - OH bond is broken whereas in hydration water molecule adds up to a substance without bond breakage.

There are four types of salts on the basis of their reactivity with water:

1. Salts of strong acids and strong bases do not hydrolyse ($\text{pH} = 7$).

Examples: NaCl , Na_2SO_4 , KNO_3 etc.

2. Salts of weak acids and strong bases hydrolyse producing basic solutions ($\text{pH} > 7$).

Examples: CH_3COONa , NaCN , Na_2S etc.

3. Salts of strong acids and weak bases hydrolyse producing acidic solutions ($\text{pH} < 7$).

Examples: CuSO_4 , NH_4Cl , NH_4NO_3 etc.

4. Salts of weak acids and weak bases hydrolyse, but the resulting solution is either neutral, acidic or basic. This depends upon the relative values of K_a and K_b of cations and anions of the salt.

The important aspects of the salt hydrolysis, discussed above, are summarised in Table 8.5.

8.5: Summarised discussed as above

Salt Type		Common Example	Ions which impart Hydrolysis	Solution pH (Nature)
Acid	Base			
Strong	Strong	NaCl , KBr	None	$= 7.0$ (Neutral)
Strong	Weak	NH_4NO_3 , NH_4Cl	Cations	< 7.0 (Acidic)
Weak	Strong	NaCN , K_2CO_3	Anions	> 7.0 (Basic)
Weak	Weak	NH_4CN , NH_4NO_2	Anions & Cations	May be equal, smaller or greater than 7.0

The student should be guided to discuss and explain the concept.

Do You Know

Hydrolysis is an important process in plants and animals. In living systems, most, biological reactions including ATP hydrolysis, take place during the catalysis of enzymes. The catalytic action of enzymes allows the hydrolysis of fats, oils, proteins and carbohydrates.

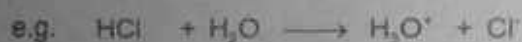
8.73 The Levelling Effect

One way to compare the strength of acids is to select a reference base (usually the solvent) and determine the extent of proton donation from the acids to the reference base. However, the reaction between any stronger acid than hydroxonium ion (H_3O^+) and water goes completely to the right. Strong acids like perchloric acid, hydrochloric acid, nitric acid and Sulphuric acid in water appear to be of equal strength. Thus, water as a base, is unable to differentiate among the relative acid strength of acids stronger than hydroxonium ion. Such inability of any solvent to differentiate among the relative strength of all acids is termed as the levelling effect. Because the solvent is said to level the strength of all the acids, making them appear identical.

The levelling effect of water can be compensated for, if a more weakly basic solvent like acetic acid is employed in place of water. Since acetic acid is a much weaker base than water, it is not easily protonated. Thus, appreciable differences in proton donation of acids are observed in acetic acid (solvent).

The relative acid strength is $\text{HI} > \text{HBr} > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$

It may be pointed out that all these acids are of identical strength in water (solvent) due to the levelling effect.



Hydroxonium ion (H_3O^+), which is acidic in nature, is formed in each case. The equal behaviour of such ions formed levels the strength of the acid.

References for additional information

- Michell J. Sienko and Robert A. Plane, Chemistry.
- John W. Hill & Synthia S. Hill, R. D., Chemistry for changing times.
- James N. Lowe, Chemistry, Industry and Environment.
- George M. Bodner and Harry L. Pardue, Chemistry an Experimental Science.



Exercise

1 Encircle the correct answer in each case:

i. Water cannot act as:

(a) Lewis acid

(c) Bronsted acid

(b) Lewis base

(d) Bronsted base

8. Acid, Bases and Salts

- ii. pH of 0.01M HCl solution is:
 (a) 10^{-2} (b) 10^{-2} (c) 2.0 (d) 1.0
- iii. An aqueous solution of ammonium chloride is:
 (a) Basic (b) Acidic (c) Neutral (d) Amphotric
- iv. An aqueous solution of which compound is basic:
 (a) Ammonium nitrate (b) Calcium chloride
 (c) Ammonium acetate (d) Potassium carbonate
- v. Which statement about acids is not correct? An acid:
 (a) Contains hydrogen ions in solution.
 (b) Contains oxygen.
 (c) Has a pH of less than 7.
 (d) Gives off carbon dioxide from a carbonate.
- vi. If a liquid has a pH of 7.
 (a) It must be colourless.
 (b) It has boiling point of 100°C .
 (c) It must be a solution.
 (d) It must be neutral.
- vii. When air is bubbled through pure water, the pH is lowered from 7.0 to 5.6, which gas in the air is responsible for this change.

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$$

 (a) Argon (b) Carbon dioxide (c) Nitrogen (d) Oxygen.
- viii. Which of the following oxides is classified incorrectly:
 (a) Zinc oxide (ZnO) amphoteric
 (b) Carbon dioxide (CO_2) acidic
 (c) Carbon monoxide neutral
 (d) Aluminium oxide (Al_2O_3) basic
- ix. If 25cm^3 of 1 mol.dm^{-3} nitric acid is added to 50cm^3 of 0.5 potassium hydroxide solution, what would be the pH of the resulting solution
 (a) 5 (b) 7 (c) 9 (d) 14
- x. If dry citric acid crystals are placed on dry litmus paper they will
 (a) turn yellow (b) turn green
 (c) turn red (d) remains unchanged
- xi. A base is a substance which will neutralise an acid which of these substances is not a base:
 (a) Aqueous ammonia (b) Copper oxide
 (c) Potassium chloride (d) Sodium carbonate
- xii. A strong acid:
 (a) Is always partially ionised when in solution.
 (b) Is always fully ionised when in solution.
 (c) Always decomposes carbonates.
 (d) Always contains oxygen.

- xiii. Which one of the following oxides dissolves in water to form acidic solution:
 (a) MgO (b) Na_2O (c) SO_2 (d) SiO_2
- xiv. When crystals of copper sulphate are heated, the colour changes from blue to white. This is caused by:
 (a) Loss of water only
 (b) Loss of water and SO_2 .
 (c) Reaction with CO_2 in the air.
 (d) Loss of water, sulphur dioxide and oxygen.
- xv. The oxide of a metal was found to react with HCl and aqueous NaOH solution. Which of the following is the best description of the oxide?
 (a) Acidic (b) Amphoteric (c) Basic (d) Neutral

SHORT QUESTIONS

- What are acidic, basic and amphoteric substances? Give one example of each substance.
- Elaborate with equations two compounds which are amphoteric in nature.
- What is Bronsted - Lowry acid-base theory? Give examples.
- What are conjugate acid-base pairs? Explain with examples.
- Define Lewis acid and Lewis bases. Give one example in each case.
- Classify each of the following as Bronsted acid or Bronsted base.
 (i) HCO_3^- (ii) HBr (iii) CH_3COO^-
Base acid Base
- Explain gastric acidity and use of anti-acid drug.
- Write briefly about the ionisation of water.
- Define pH what are the values of pH for acidic, basic and neutral solutions.
- Define K_a and pK_a and their applications.
- Explain curdling of milk with lemon juice.
- What are K_b and pK_b and their applications?
- What is an iodised salt? What is its use in practical life?
- What is the relationship between K_a and K_b ?
- Calculate concentrations of ions of slightly soluble salts.
- Give two examples of a buffer solution.
- Elaborate the ionization equation of water. How does it lead to the ion-product constant of water? Describe an important application of the ion-product of water.
- What are buffer solutions? Elaborate with suitable examples, their significance in acid base reactions. Write three common applications of buffer solutions.
- Write detailed notes on each of the followings:
 (a) Conjugate acid base pairs (b) pK_a (c) pK_b (d) Relative strength of acids.

- 6 What is hydrolysis? Discuss in detail, the behaviour of each of the following salts in their aqueous solutions.
- (a) K_2CO_3 (b) NH_4Cl (c) $NaNO_3$
- 7 (a) Calculate the pH of formic acid-sodium formate buffer solution containing 1.0 mole of each component. (Ans: 3.7447)
- (b) What will be the pH of the solution after addition of 0.10 mole of hydrochloric acid gas to $1.01 dm^3$ volume of the buffer solution in part (a). Assume that the volume of solution remains unchanged on addition of hydrochloric acid (K_a for formic acid is 1.8×10^{-4}). (Ans: 3.6997)
- 8 (a) Calculate the H^+ ion concentration of an aqueous solution having pH 10.6 (Ans: 2.5×10^{-11} moles/ dm^3)
- (b) An aqueous solution contain 1.0×10^{-9} moles/ dm^3 of hydronium ions. Calculate the pOH of this solution (Ans: 5.0)
- 9 (a) What is acid dissociation constant? How is it related to pK_a ? Write equation to elaborate.
- (b) Define and briefly describe the levelling effect of water in acid-base reactions.
- 10 (a) What is hydrolysis? Write the equations of hydrolysis equilibrium for each of the followings:
- (i) Li^+ (ii) NH_4^+ (iii) CN^-
- (b) Write a unique property of a buffer solution. What types of acids are required to prepare buffer solutions? Name two such acids.



10

SOLUTIONS AND COLLOIDS



This is a 12 days unit

After completing this lesson, you will be able to:

- Define hydrophilic and hydrophobic molecules
- Express solution concentration in terms of mass percent, molality, parts per million, billion and trillion and mole fraction.
- Define the term colligative.
- Define the term water of hydration.
- Describe the role of solvation in the dissolving process.
- Distinguish between the solvation of ionic species and molecular substances.
- List the characteristic of colloids and suspensions that distinguish them from solutions.
- Explain the nature of solutions in liquid phase giving examples of completely miscible, partially miscible and immiscible liquid-liquid solution.
- Describe on a particle basis why a solution has a lower vapour pressure than the pure solvent.
- Explain on a particle basis how the addition of a solute to a pure solvent causes an elevation of the boiling point and depression of the freezing point of the resultant solution.
- Explain concept of solubility and how it applies to solution saturation.
- Explain the effect of temperature on solubility and interpret the solubility graph.



Reading

INTRODUCTION

Most of the substances we encounter more often in daily life are mixtures. For example milk, wood, air, gasoline etc. are mixtures of substances. Such substances have properties different from those of the pure material they contain. Recall from grade IX-X knowledge that any mixture has two defining characteristics, its composition is variable and it retains some properties of its components. In this chapter we focus on two extremely common types of mixtures, solutions and colloids. We will discuss role of intermolecular forces in their formation. We will examine equilibrium nature of solubility and will discuss how temperature and pressure affect it. We have already

learned various types of solutions in the grade IX-X. Here we will discuss ways of expressing concentration. We will also discuss some important properties of solutions which do not depend on the nature of solute and daily life application of such properties.

10.1. GENERAL PROPERTIES OF SOLUTIONS

A sample of matter having a fixed composition and uniform properties throughout is called a phase. For example pure sample of water under standard conditions exists as

single liquid phase. The properties of water e.g. density, vapour pressure etc are uniform throughout this liquid phase. When a small quantity of sugar or common salt dissolves in it, the entire sample remains a single phase. The composition and properties of this new phase are different from those of pure water. This is a mixture since it contains two different substances. Such a mixture is said to be homogeneous, because its properties are uniform throughout the liquid.

A homogeneous mixture of two or more pure substances, which has uniform composition throughout is called solution. Do you think, air is a solution?

10.1.1. Hydrophilic and Hydrophobic Molecules

Dissolving solid solutes in water is very common. We dissolve salt in water used to cook vegetables, meat, pulses etc. Particles of solute (atoms, ions, or, molecules) interact with the solvent molecules and become part of the structure of the solvent during the dissolving process. For example, when glucose is dissolved in water, the crystalline structure of glucose is broken down by the water molecules. When totally dissolved, glucose molecules are evenly distributed throughout the water. Oceans contain many dissolved solid substances such as sodium chloride, sodium bromide, magnesium chloride etc.

There are some substances that do not dissolve in water. For instance substances like benzene, cyclohexane, oils etc. do not dissolve in water. This is because these substances have non-polar molecules which do not have any interaction with water molecules. Therefore, molecules can be hydrophilic or hydrophobic in nature.

Hydro mean water, philic means loving. So hydrophilic literally means water loving. Molecules that are miscible with water are known as hydrophilic molecules. Such molecules can form hydrogen bond with water molecules. For example, molecules of methanol, acetone, acetic acid etc. are called hydrophilic molecules. Since phobic means disliking, therefore hydrophobic literally mean water disliking. Molecules that do not dissolve in water are known as hydrophobic molecules. For example, molecules of organic fats and oils are called hydrophobic molecules.

10.1.2 Nature of Solution in Liquid phase (Like dissolve like) (bond)

Solutions of liquids in liquids may be divided into three classes.

- (a) Completely miscible (b) Partially miscible (c) Immiscible.

Completely Miscible Liquids

Liquids which are miscible in all proportions are called completely miscible. For instance water and methanol, acetone and water, benzene and cyclohexane are completely miscible liquid pairs. Substances that dissolve in each other possess similar types of inter-molecular interactions. For example water and methanol are miscible because molecules in the pure liquids and their mixtures form hydrogen bonds. The degree of hydrogen bonding in the solution is same as that in the pure liquids. Benzene and cyclohexane are completely miscible because the



The student should be guided to recall information.

molecules in the pure liquids and their mixtures interact through London dispersion forces. These dispersion forces between benzene and cyclohexane are about the same as those in pure liquids.

Partially Miscible Liquids

Liquids that dissolve in each other to a very small extent are called partially miscible liquids. On mixing such liquids two layers are formed. Each layer is a saturated solution of the other liquid. For example ether and water are partially miscible liquids. The mutual solubilities of these solutions change by temperature changes.

Typical examples of such systems are:-

- (i) Phenol-water
- (ii) Aniline-water
- (iii) Aniline-n-hexane
- (iv) Nicotine-water

Phenol-water system

When equal volumes of phenol and water are mixed into each other, two liquid layers are formed. The lower layer consists of a small amount of water dissolved in phenol, while the upper layer consists of small amount of phenol dissolved in water. It is observed that at 25°C upper layer is 5% solution of phenol in water and the lower layer is 30% water in phenol. This means water is solute in lower layer and phenol is solute in the upper layer. Such solutions are called conjugate solutions. As the temperature increases, the mutual solubility of two liquids increases. Water starts moving from upper to the lower layer and phenol from lower layer to the upper layer. Thus composition of both the layers changes. When the temperature finally reaches 65.9°C , the composition of both the layers become identical. Each layer contains 34% phenol and 66% water. Above this temperature two solutions merge into one another and two liquids become completely miscible in all proportions. The temperature at which two conjugate solutions merge into one another is called critical solution temperature or upper consolute temperature. For example:

Critical solution temperature for water-aniline system is 167°C with 15% water and that for aniline-hexane is 59.6°C with 52% aniline. And that for water-phenol is 65.9°C with 34% phenol.

Completely Immiscible Liquids

What happens when you mix oil in water?

Liquids which do not dissolve into each other in any proportion at any temperature are called completely immiscible. For instance water and benzene, carbon disulphide and water, cyclohexane and water. Benzene, carbon disulphide or cyclohexane are non-polar in nature. The only forces of attraction between their molecules are dispersion forces. In water hydrogen bonds are much stronger than dispersion forces. Since hydrogen bonds cannot be disrupted by the molecules of benzene, carbon disulphide or cyclohexane, these liquids are immiscible with water.

The student should be guided to distinguish between different parts of topics.

10.1.3 Dissolution Process

When a solute is added in a suitable solvent, it dissolves forming a solution. In the formation of a solution three types of interactions are involved. These are solute - solute, solvent-solvent and solute-solvent interactions. A solution forms only when the interactions between solute-solvent molecules are equal to or greater than the interactions between solute-solute and solvent-solvent molecules. This means, the process of dissolution can occur only when the interactions that hold together solute particles are weakened appreciably by the solute-solvent interactions. The speed with which a solute dissolves in a solvent is called dissolving rate. Four factors influence the rate at which substances dissolve. (1) Particle size (2) Temperature (3) Solution concentration (4) Stirring.

When a sugar cube is placed into water, it dissolves slowly than does an equal amount of finely granulated sugar. A sugar cube exposes less surface area to the water molecules than do the tiny particles of granulated sugar. Inner regions of cube dissolve only after the outer layers are in solution. There are fewer unexposed particles when sugar is granulated, so it dissolves faster. Thus, to increase the rate of dissolving, large piece of solid must be grinded into small particles.

Temperature is another factor which changes the rate at which solutes dissolve in a solvent. At higher temperature, increased molecular motion increases the interaction of solute and solvent particles which increases the dissolving rate.

As the concentration of solute in solution increases, the time needed for more solute to dissolve increases. Initially the dissolving rate is maximum. When the first solute is added to the solvent. With each addition of solute, the dissolving rate decreases until no more solute is observed to dissolve. At this stage solution is said to be saturated. Any addition of solute to a saturated solution remain un-dissolved and settle to the bottom of the container.

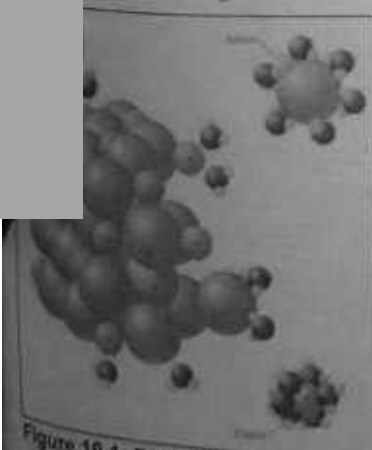


Figure 10.1: Dissolving of ammonium nitrate crystal in water

Stirring a solution increases the rate at which a solid dissolves decreasing the concentration of solute in the immediate region surrounding the solid solute. Stirring also increases the amount of exposed solute surface to the solvent.

10.1.4 Solvation of Ionic and Molecular Substances

Ionic solids are soluble only in solvents having polar molecules. When an ionic compound is dissolved in a polar solvent, it splits up into its ions. For instance, when NH_4NO_3 dissolves in water the resulting solution contains NH_4^+ and NO_3^- ions floating around independently. Solvent molecules surround these ions by directing their negative poles towards

The student should be guided to explain the concepts.

positive ions and their positive poles towards negative ions. This interaction is called as ion-dipole interaction (see figure 10.1). Circles with positive sign represent NH_4^+ ions and circles with negative sign represent NO_3^- ions. Process of solvation of ionic and molecular substances is similar in the sense that in both the cases the process of solvation involves the disruption of solute particles from the crystal lattice. Then these particles are surrounded by solvent molecules. However, the heat of solvation in both the cases is much different since ion-dipole interactions are much stronger than dipole-dipole or dispersion forces, heat of solvation for ionic species is generally larger than those for molecular solvents.

Molecular solids are held together by dispersion forces, dipole-dipole forces and sometimes hydrogen bonds. Such solids dissolve readily in solvents with similar types of intermolecular forces. For example when a polar molecular substance is mixed with a polar solvent. Polar ends of solvent molecules interact with the opposite polar ends of molecules of solute and break attractive forces between them. Finally solvent molecules surround these molecules. The interaction is called dipole-dipole interaction.

The process in which solvent molecules interact and surround solute ions or molecules is known as **solvation**. When water is the solvent, this process is known as **hydration**.

10.1.5 Role of Solvation in the Dissolving Process

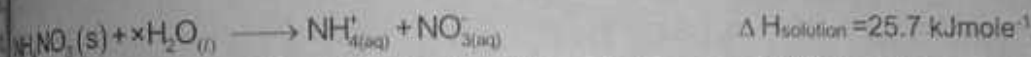
Solution making process is accompanied by either the absorption or evolution of heat. Energy change in the formation of a solution depends upon three types of interactions between solute-solute, solvent-solvent and solute-solvent particles. In the formation of solution interactions between solute particles are broken. At the same time solvent molecules also move apart to accommodate the solute particles. Since energy is needed to break interactions. Therefore, both these processes are endothermic. Simultaneously interactions between the particles of solute and solvent are established i.e., solvation occurs. Solvent molecules surround solute particles from all sides. In these interactions energy is released, so it is exothermic. Thus the strength of these two types of interactions determines whether the process of dissolution is endothermic or exothermic.

Thus when a solute dissolves in water, attractive forces among these solute particles must be overcome to break solute particles from the solid lattice. A strong force must bind these separated solute particles to water molecules in the solution. Therefore, heat of solution measures the net energy flow that occurs as a substance dissolves. The energy needed to break solute particles is equal to lattice energy of solute ($\Delta H_{\text{lattice}}$). On the other hand the energy released when solute particles bind to the water molecules in the solution is called heat of hydration (ΔH_{hyd}). Heat of hydration increases with increasing charge on the ions and decreases with increasing size of ions. For other solvents this energy is known as heat of solvation. Heat of solution includes both the energy needed to move solvents molecules

part and energy release when they surround solute particles. Thus, heat of solution $\Delta H_{\text{solution}}$ is the difference in $\Delta H_{\text{lattice}}$ and ΔH_{hyd} .

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} - \Delta H_{\text{hyd}}$$

Because of the different attractive forces in both solute and solution, heats of solution vary from significantly exothermic to significantly endothermic. If the crystal binds solute particles more tightly than the solution, solute must absorb energy as it dissolves and we have an endothermic solution process. When this $\Delta H_{\text{solution}}$ is very large, the solute is unlikely to be soluble. But if this $\Delta H_{\text{solution}}$ is moderately positive, then solute dissolves. For example, when ammonium nitrate dissolves in water 25.7 kJmol^{-1} energy is absorbed and the flask becomes cold. This is because crystal binds NH_4^+ and NO_3^- ions more tightly than the solution.



On the other hand, if solution binds solute particles more tightly than the crystal, energy is released as the solute dissolves and we have an exothermic solution process.

For example, when NaOH dissolves in water 44.5 kJmol^{-1} energy is released and the flask becomes hot



Thus solution process can be endothermic or exothermic depending upon the difference in the lattice energy for solute and heat of solvation for solute particles. Other examples are given below



The values of standard enthalpies of solution of some ionic solids in water are given in Table 10.2

Table 10.2: Enthalpies of Solutions of some ionic solids.

Substance	Enthalpy of Solution (kJ mol^{-1})
LiCl	-37.0
NaCl	+2.98
KCl	+17.2
KI	+20.3
NH_4NO_3	+25.7
AlCl_3	-321.0

Daily Life Applications of Heat of Solution

Instant hot and cold packs are in common use today. Cold packs are used for the treatment of injuries and reduction of swelling. Hot packs are used for instant warmth for hikers and skiers and treatment of pulled muscles. These packs are excellent examples of basic science producing a technologically useful product. These packs are based on heat of solutions. These packs contain two separate compartments. One contains water and the other contains a salt,

NH_4NO_3 for cold packs and CaCl_2 or MgSO_4 for hot packs. When required these packs are kneaded, the wall between the compartments breaks, allowing the salts to mix with water. Heat is absorbed in cold packs and released in hot packs. Gradually these packs attain room temperature. For the amount of heat absorbed or released in these packs, see section 10.1.5.

10.1.6 Water of Hydration

A crystalline substance which has associated with each formula unit a definite number of water molecules is called a hydrate. Such water molecules are called water of crystallization or water of hydration. The water molecules that combine with compounds as they are crystallized from aqueous solution are called water of crystallization or water of hydration. For example,

- | | |
|---|--|
| (i) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | (ii) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ |
| (iii) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | (iv) $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ |
| (v) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ | |

How many moles of water are present in hydrated copper sulphate.

The percentage of water in a hydrate can be determined. For this purpose a known mass of hydrate is heated to expel water completely. Mass of anhydrous solid is determined. Difference in the two masses gives the mass of water present. From these masses, percentage of water in the hydrate is determined. An ion having higher charge density has greater ability to attract water molecules. In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, the charge density of Cu^{++} ion is greater than that of SO_4^{--} ion. Thus Cu^{++} ion has greater ability to attract water molecules than SO_4^{--} ion. That is why out of five water of hydration four are associated with Cu^{++} ion and only one with SO_4^{--} ion. In hydrates, although new bonds between ions and water molecules are formed but no hydrogen oxygen bond of water is broken.

$$\text{Percent water in a hydrate} = \frac{\text{mass of water in the hydrate}}{\text{mass of hydrate}} \times 100$$

Example 10.1

250g of $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ on heating produced 159.82g CuSO_4 . Calculate the percent of water in the $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$. Also determine the value of x.

Problem solving strategy

1. Find the mass of hydrate by subtracting mass of anhydrite from that of hydrate.
2. Find % water in hydrate using formula.
3. Find the value of x using formula.

Solution

Mass of $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$	=	250g
Mass of CuSO_4	=	159.82g

10. Solution and Colloids

255

$$\begin{aligned}\text{Mass of water in the hydrate} &= 250 - 159.82 \\ &= 90.18\text{g} \\ \text{Percent of water in the hydrate} &= \frac{90.18\text{g}}{250\text{g}} \times 100 \\ &= 36.07\%\end{aligned}$$

$$\begin{aligned}X = \text{No. of moles of water} &= \frac{\text{Mass of water in hydrate}}{\text{molar mass of water}} \\ &= \frac{90.18\text{g}}{18\text{g/mole}} \\ X &= 5.01 \\ X &= 5\end{aligned}$$

Do You Know

One of the water's most valuable properties is its ability to dissolve many substances. Without this property, many things on earth would be different. For example the oceans would not be salty. Plants and animals, which depend on moving dissolved substances into and out of their cells, would not exist.

10.1.7 Concept of Solubility

How can you sweeten drinks such as tea?

When a small amount of solute is mixed in excess of water, it dissolves to form a solution. If a little more solute is added it will also dissolve. Such a solution which can dissolve more solute under existing conditions is called **unsaturated solution**. As more and more solute is added, a stage is reached where further dissolving seems to cease leaving solid solute at the bottom of the container. Such a solution which contains maximum amount of dissolved solute under existing conditions is called **saturated solution**. The maximum amount of solute that dissolves in the given quantity of a solvent under given conditions is called **solubility**. Solubility is commonly expressed in number of grams of solute per cm^3 of solution or in terms of number of moles of solute per dm^3 of solution.

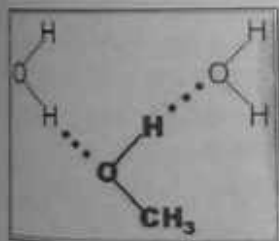


Fig 10.2: H-bonding between water and methanol

On molecular level a saturated solution is in equilibrium with excess of solute. At equilibrium the rate of solute going into the solution equals the rate of solute returning from the solution.



In a saturated solution dissolving of solute in fact continues. At the same time many dissolved particles moving freely in solution strike the solid solute. Such particles are recaptured by the solid solute present at the bottom of the container. Such particles are thus re-crystallized. A stage is reached when a dynamic equilibrium is established between dissolved and undissolved solute.

A general rule useful for predicting solubilities is "like dissolves like." Substances which have similar structures and intermolecular forces tend to be soluble. While substances which have dissimilar structures and intermolecular forces are insoluble.

The student must be guided to argue about the information.

For instance, water and methanol have similar structures and have hydrogen-bonding between their molecules. They can form hydrogen bonds with each other, when they are mixed. See Fig 10.2. Thus water and methanol are miscible.

Molecules of benzene, C_6H_6 and carbon tetrachloride CCl_4 are non-polar and have London dispersion forces between their molecules. When these two liquids are mixed, their molecules attract each other with London dispersion forces, thus these are miscible liquids. Think what will happen when CCl_4 or Benzene is mixed with water?

Ionic solids have a crystal lattice structure composed of oppositely charged ions. When an ionic solid e.g. NaCl is placed in water which is a polar solvent. These ions are attracted by polar molecules. Water molecules break the crystal lattice of Na^+Cl^- and then surround the resulting Na^+ and Cl^- ions. These ions are called hydrated ions.

But when NaCl crystals are placed in CCl_4 or C_6H_6 . Non-polar molecules of these liquids are unable to attract ions in Na^+Cl^- and cannot break apart the crystal lattice. Thus NaCl is insoluble in these solvents. Think, what will happen when solid NH_4NO_3 , an ionic solid is placed in water?

Self Check Exercise 10.1

Which solvent, liquid ammonia, NH_3 or benzene, C_6H_6 is more likely to dissolve each of the following solute. Give reasons?

- (a) AgCl (b) Wax (c) H_2O (d) NH_4OH

Effect of Temperature on Solubility

Generally, an increase in temperature increases solubility of a solid in a liquid. At higher temperature greater masses of solutes dissolve in a fixed mass of water than at lower temperature. A curve drawn between solubility and temperature is called **solubility curve** (see figure 10.3). The solubilities of solid solutes generally increase with the increase in temperature. However this is not always the case. The solubilities of some solids e.g. Na_2SO_4 and $Ca_2(SO_4)_2$ decrease with increasing temperature. Some substances like NaCl have relatively constant solubility with increasing temperature.

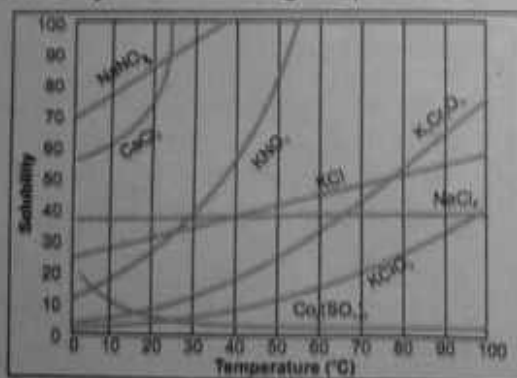


Figure 10.3: Solubility curves, which substance has higher solubility at room temperature?

The variation of solubility with temperature can be predicted from the enthalpy of solution. If $\Delta H^\circ_{\text{Soln}}$ is negative, the solubility of solute decreases as the temperature increases. But if $\Delta H^\circ_{\text{Soln}}$ is positive, the solubility increases with temperature.

Solubility of KNO_3 rapidly increases with increase in temperature, this is because it has large positive value of $\Delta H^\circ_{\text{Soln}}$ (+36 kJ/mole) the solubility of NaCl does not vary much with temperature because of relatively small magnitude of $\Delta H^\circ_{\text{Soln}}$ (+3 kJ/mole).

10. Solution and Colloids

It is generally observed that the solubility of a gas decreases with increasing temperature. The dissolving of gases in liquids can be understood in terms of two processes (a) the condensation of the gas which is exothermic and (b) the creation of holes in the liquid to accommodate the condensed gas molecules, it is endothermic. Because of the open structure of water, little work is required to accommodate gas molecules, this means dissolving process is exothermic. Thus solubility of gases in water decrease with temperature.

Self Check Exercise 10.2

Consult solubility curve shown in figure 10.3 and explain the following

1. Solubility of $\text{Ce}_2(\text{SO}_4)_3$ and that of KClO_3 is positive or negative.

2. Solubility of CaCl_2 is greater or lesser than that of NaNO_3 at 20°C .

Indicate the temperature at which solubilities of NaCl and KCl are same.

Which of the following salts has rapid increase in solubility with the increase in temperature:

(a) CaCl_2 (b) $\text{K}_2\text{Cr}_2\text{O}_7$

Effect of Pressure on Solubility

Pressure has negligible effect on the solubility of solids or liquids. On the other hand it does significantly increase the solubility of a gas. At a given temperature, the solubility of gases which do not react with the solvent are directly proportional to the partial pressures of the gases above the solution. This relationship is known as **Henry's Law**. It is obeyed most accurately by dilute solutions of gases: Henry's law can be understood from Fig. 10.4.

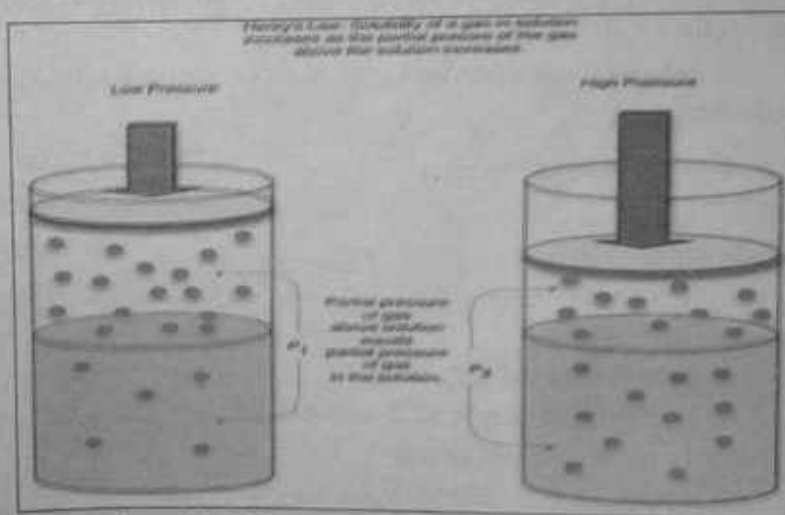


Figure 10.4: Schematic representation of Henry's law

Equilibrium between the gas above a liquid and the dissolved gas within the liquid is reached when the rates of evaporation and condensation of gas molecules become equal. (Fig. 10.4). When the pressure is suddenly increased by pushing the piston, the number of molecules per unit volume increase in the gaseous state, this causes an increase in the rate at which the gas enter the solution, so the concentration of the dissolved gas increases. The greater gas concentration in the solution causes an increase in the rate of evaporation, until a new equilibrium is reached.

Carbonated drinks are bottled at high pressure of carbon dioxide. When the cap is removed, the effervescence results from the fact that the partial pressure of carbon dioxide in the atmosphere is much less than used in the bottling process. As a result, the equilibrium quickly shifts to one of the lower gas solubility. This causes effervescence.

10.2. CONCENTRATION UNITS

We sometimes speak of dilute or concentrated solutions, but these terms have no precise meaning. A dilute solution is one which contains relatively small amount of solute per unit volume of solution. Whereas a concentrated solution is one which contains relatively greater amount of solute per unit volume of solution. We need to define solution composition more precisely in order to perform calculations. The amount of solute, solvent and solutions may be expressed by volume, mass or number of moles. Therefore, there are various types of concentration units. Some of these are given below.

1. Mass Percent

It is defined as the mass of solute present in 100g of solution. It is also referred as percent weight / weight.

$$\text{Mass Percent} = \frac{\text{grams of solute}}{\text{grams of solution}} \times 100$$

15% NaCl solution means 15g of NaCl dissolved per 100 g of solution or 85g of water.

Example 10.2

Calculate mass percent of a solution containing 10g sugar dissolved in 100g of water.

Solution

$$\begin{aligned} \text{Mass Percent} &= \frac{\text{grams of sugar}}{\text{grams of solution}} \times 100 \\ &= \frac{10\text{g sugar}}{(10\text{g sugar} + 100\text{g water})} \times 100 \\ &= 9.09\% \end{aligned}$$

2. Percent weight by volume

It is the mass of solute dissolved per 100 part by volume of solution. In this case volume of solvent is not exactly known.

$$\text{Percent w/v} = \frac{\text{Mass of solute (g)}}{\text{vol. of solution (cm}^3\text{)}} \times 100$$

For example, a 10% (w/v) NaCl solution contains 10g NaCl dissolved in 100 cm³ of solution.

3. Percent volume by volume

It is the volume of solute dissolved per 100 parts by volume of solution. In such solutions volumes of solute and solvent may not be necessarily equal to the volume of solution

$$\text{Percent v/v} = \frac{\text{cm}^3 \text{ of solute}}{\text{cm}^3 \text{ of solution}} \times 100$$

For example a 5% (v/v) ethanol solution means 5cm³ ethanol dissolved per 100 cm³ of solution

4. Percent volume by weight

The volume of a solute dissolved per 100g of solution is called percent volume by weight. In this case total volume of solution is not known.



The student should be guided to recall information

10. Solution and Colloids

For example, a 5% (v/w) Ethanol contains 5 cm³ ethanol per 100g of solution.

$$\% \text{ v/w} = \frac{\text{volume of solute (cm}^3\text{)}}{\text{Mass of solution (g)}} \times 100$$

5. Molarity (M)

It is defined as the number of moles of solute dissolved per dm³ of solution. Note that the reference volume is that of solution and not the pure solvent. If 0.5 mole of NaOH (20g) is dissolved in enough water to make one dm³ of solution, 0.5 molar or 0.5 M NaOH solution is obtained.

$$M = \frac{\text{moles of solute}}{\text{dm}^3 \text{ of solution}}$$

depend upon temperature because when temperature increases, volume also increases.

$$M = \frac{\text{grams of solute}}{\text{molar mass of solute} \times \text{dm}^3 \text{ of solution}}$$

Example 10.3

What is the molarity of a solution of 0.25g of NaHCO₃ in 100 cm³ of solution.

$$\begin{aligned} \text{Mass of NaHCO}_3 &= 0.25\text{g} \\ \text{Molar mass of NaHCO}_3 &= 23+1 + 12 + 16 \times 3 \\ &= 84\text{g / mole} \\ \text{Volume of solution} &= 100 \text{ cm}^3 \\ &= 100/1000 = 0.1 \text{ dm}^3 \\ \text{Molarity} &= \frac{\text{grams of NaHCO}_3}{\text{molar mass of NaHCO}_3 \times \text{dm}^3 \text{ of solution}} \\ &= \frac{0.25\text{g}}{84 \text{ g / mole} \times 0.1 \text{ dm}^3} \\ &= 0.0298 \text{ M} \end{aligned}$$

6. Molality (m)

It is defined as the number of moles of solute dissolved per kilogram of solvent. For example when 58.5g NaCl (1 mole) is dissolved in one kilogram of water, the resulting, solution would be one molal or 1m NaCl solution.

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

Example 10.4

Ethanol is an excellent organic solvent. It is used to prepare tinctures and in the extraction of medicinal compounds from plants. For this purpose either pure ethanol or its aqueous solutions are used. A solution is prepared by mixing 1.00g of ethanol (C₂H₅OH) with 100g of water. Calculate molality of this solution.

$$\begin{aligned} \text{Mass of ethanol} &= 1.00\text{g} \\ \text{Molar mass of ethanol} &= 12 \times 2 + 1 \times 6 + 16 \\ &= 46\text{g/mole} \end{aligned}$$

$$\begin{aligned}
 \text{Moles of ethanol} &= \frac{1.00\text{g}}{46\text{g/mole}} \\
 &= 2.17 \times 10^{-2} \text{ mole} \\
 \text{Mass of water} &= 100\text{g} \\
 &= 100/1000 = 0.1 \text{ kg} \\
 \text{Molality of solution} &= \text{moles of } \text{C}_2\text{H}_5\text{OH} / \text{kg of water} \\
 &= 2.17 \times 10^{-2} \text{ mole} / 0.1 \text{ kg} \\
 &= 0.217 \text{ m.}
 \end{aligned}$$

Notice that molality is independent of temperature whereas molarity depends on temperature. This is because molarity is based upon volume of solution. As the temperature increases, the amount of solute remains constant but the volume of solution increases slightly, thus molarity decreases slightly.

Self Check Exercise 10.3

Any fluids infused intravenously into an individual must be isotonic with the blood cells and the blood plasma. Such infusions are either 5% dextrose (glucose) or 0.9% normal saline. The first solution is composed of 5.0 gram of glucose per 100 cm³ of solution and the other of 0.9 gram NaCl per 100 cm³ of solution. Calculate the molarity of these intravenous solutions.

(Ans: 0.28M, 0.15M)

7. Mole Fraction (X)

It is sometimes necessary to use a concentration unit in which the amount of all the solution components are described on a number basis. This can be done through mole fraction concentration unit.

It is defined as the ratio of the number of moles of a given component to the total number of moles of solution. Suppose a solution contains n_A and n_B moles of two components A and B. Mole fraction of each component is given by

$$\text{Mole fraction of component A} = X_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of component B} = X_B = \frac{n_B}{n_A + n_B}$$

Example 10.5

An aqueous solution containing 100g ethanol per dm³ of solution has a density of 0.984 g cm⁻³. Calculate mole fraction of each component of solution.

Solution

$$\begin{aligned}
 \text{Volume of solution} &= 1\text{dm}^3 = 1000 \text{ cm}^3 \\
 \text{Mass of ethanol} &= 100\text{g} \\
 \text{Mass of solution} &= \text{Density} \times \text{Vol of solution of solution} \\
 &= 0.984 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 \\
 &= 984\text{g} \\
 \text{Mass of water (solvent)} &= 984\text{g} - 100\text{g}
 \end{aligned}$$

$$\begin{aligned}
 &= 884\text{g} \\
 \text{No of moles of H}_2\text{O} &= \frac{884\text{g}}{18\text{g / mole}} \\
 &= 49.1 \text{ mole} \\
 \text{No. of moles of ethanol} &= \frac{100\text{g}}{46\text{ g / mole}} \\
 &= 2.17 \text{ mole} \\
 \text{Total No. of moles in solution} &= 49.1 + 2.17 \\
 &= 51.27 \text{ mole} \\
 X_{\text{H}_2\text{O}} &= \frac{49.1 \text{ mole}}{51.27 \text{ mole}} \\
 &= 0.958 \\
 X_{\text{ethanol}} &= \frac{2.17 \text{ mole}}{51.27 \text{ mole}} \\
 &= 0.042
 \end{aligned}$$

8. Parts per million (ppm)

It is defined as the number of parts by weight (or volume) of a solute per million parts by weight (or volume) of the solution.

$$\text{ppm} = \frac{\text{Mass or volume of solute}}{\text{Mass or volume of solution}} \times 10^6$$

9. Parts per billion (ppb)

It is defined as the number of parts by weight (or volume) of a solute per billion parts by weight (or volume) of the solution.

$$\text{ppb} = \frac{\text{Mass or volume of solute}}{\text{Mass or volume of solution}} \times 10^9$$

10. Parts per trillion (ppt)

It is defined as the number of parts by weight (or volume) of a solute per trillion parts by weight (or volume) of the solution.

$$\text{ppt} = \frac{\text{Mass or volume of solute}}{\text{Mass or volume of solution}} \times 10^{12}$$

Rare components of a solution are expressed by ppm, ppb and ppt. A pollutant concentration of 1 ppm in the atmosphere means that out of one million molecules of air there is one molecule of the pollutant, whereas 1 ppb concentration of it means that out of one billion molecules of air there is one molecule of that pollutant.

Example 10.6

An atmospheric chemist reports that one dm^3 of air in an urban area contained $3.5 \times 10^{-4} \text{ cm}^3$ of CO. What was the concentration of CO in ppm?

$$\begin{aligned}
 \text{ppm} &= \frac{\text{Volume of CO (cm}^3\text{)}}{\text{Volume of air (cm}^3\text{)}} \times 10^6 \\
 &= \frac{3.5 \times 10^{-4} \text{ cm}^3}{10^3 \text{ cm}^3} \times 10^6 \\
 &= 0.35 \text{ ppm.}
 \end{aligned}$$

Example 10.7

If the concentration of ozone in atmosphere reaches 0.5 ppb. What mass of ozone would be present per kg of air.

Solution

$$\begin{aligned}
 \text{ppb} &= \frac{\text{Mass of ozone (g)}}{\text{Mass of air (g)}} \times 10^9 \\
 0.5 &= \frac{\text{Mass of ozone}}{1000 \text{ g}} \times 10^9 \\
 \text{Mass of ozone} &= \frac{0.5 \times 1000}{10^9} \\
 &= 0.5 \times 10^3 \times 10^{-9} \\
 &= 5 \times 10^{-7} \text{ g}
 \end{aligned}$$

Self Check Exercise 10.4:

1. Calculate the ppm by mass of calcium in a 2.5g tablet that contains 500mg calcium. (Ans: 0.2×10^6 ppm)
2. Waste water from a cement factory contains 22mg Ca^{+2} ions and 0.006g Mg^{+2} ions per kg of solution. Calculate the concentration of both these ions in ppm. (Ans: 22ppm, 6ppm)
3. Gold occurs in sea water at an average concentration of 1.09×10^{-2} ppb. How many kg of water must be processed to recover 1gm of Gold. (Ans: 9.17×10^7 kg)

10.2.1 Inter Conversion of Various Concentration Units of Solution.

Sometimes we get prepared solutions whose molarity is given, but we need its w/w percentage or molality. For this purpose, we need to convert one unit of concentration into other. How it can be done? It is explained by the following examples.

Example 10.8

Calculate the molality of 15% (w/w) glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution.

Solution

Since solution of glucose is 15% w/w

$$\text{Mass of glucose} = 15\text{g}$$

$$\text{Mass of solution} = 100\text{g}$$



The student should be guided to interpret information.

10. Solution and Colloids

$$\begin{aligned}
 \text{Mass of water} &= 100\text{g} - 15\text{g} \\
 &= 85\text{g} \\
 &= 85/1000 = 0.085\text{ kg} \\
 \text{Molar mass of glucose} &= 12 \times 6 + 1 \times 12 + 16 \times 6 \\
 &= 180\text{ g / mole} \\
 \text{Molality} &= \frac{\text{Mass of solute (g)}}{\text{Molar mass of solute g / mole} \times \text{Mass of solvent (kg)}} \\
 \text{Molality} &= \frac{15\text{ g}}{180\text{ g / mole} \times 0.085\text{ kg}} \\
 \text{Molality} &= 0.98\text{ moles per kg.} \\
 \text{Molality} &= 0.98\text{ m}
 \end{aligned}$$

Example 10.9

Sulphuric acid is known as king of chemicals it is used in the manufacture of many chemicals, drugs, dyes, plastics, paints, disinfectants, explosives, synthetic fibres etc. It is prepared commercially by contact process and is normally 98% by weight. If its density is 1.84 g cm^{-3} , what is its molarity.

Solution

$$\begin{aligned}
 \text{Molar Mass of } \text{H}_2\text{SO}_4 &= 1 \times 2 + 32 \times 1 + 16 \times 4 \\
 &= 98\text{ g/mole}
 \end{aligned}$$

$$\text{Percentage of } \text{H}_2\text{SO}_4 \text{ solution} = 98\%$$

$$\text{Density of } \text{H}_2\text{SO}_4 \text{ solution} = 1.84\text{ g cm}^{-3}$$

$$1\text{ cm}^3 \text{ of } \text{H}_2\text{SO}_4 \text{ solution contains } 1.84\text{ g } \text{H}_2\text{SO}_4 \text{ solution}$$

$$1000\text{ cm}^3 \text{ g } \text{H}_2\text{SO}_4 \text{ solution would}$$

$$\begin{aligned}
 \text{have} &= 1.84 \times 1000 \\
 &= 1840\text{ g } \text{H}_2\text{SO}_4 \text{ solution}
 \end{aligned}$$

Of this total mass 98% is H_2SO_4

$$\begin{aligned}
 \text{Mass of } \text{H}_2\text{SO}_4 \text{ in solution} &= 1840 \times 98 / 100 \\
 &= 1803.2\text{ g}
 \end{aligned}$$

$$\begin{aligned}
 \text{Moles of } \text{H}_2\text{SO}_4 \text{ in solution} &= 1803.2\text{ g} / 98\text{ g/mole} \\
 &= 18.4\text{ moles}
 \end{aligned}$$

Since solution has 18.4 moles of H_2SO_4 per 1000 cm^3 or 1 dm^3 of solution, the molarity of this solution is 18.4 M.

Example 10.10

Commercial HCl is 12 molar (density $= 1.17\text{ g cm}^{-3}$). Calculate the mass percent of HCl in this solution.

The student should be guided to operate information in practical uses.

Solution

$$\text{Molarity of HCl} = 12 \text{ M}$$

$$\text{As } d = m / v$$

$$m = d \times v$$

Thus mass of HCl solution present in its 1000 cm^3 (1 dm^3) would be

$$1.17 \text{ g / cm}^3 \times 1000 \text{ cm}^3 = 1170 \text{ g}$$

$$\text{Molar mass of HCl} = 1 + 35.5$$

$$= 36.5 \text{ g/mole}$$

As HCl solution is 12M,

$$\text{Mass of HCl in solution} = 12 \times 36.5$$

$$= 438 \text{ g}$$

$$\text{Mass percent of HCl} = \frac{438 \text{ g} \times 100}{1170 \text{ g}}$$

$$= 37.44\%$$

Often more concentrated solutions are diluted to obtain less concentrated solutions. Such dilutions are done after calculating the amount of water that is mixed with the more concentrated solution to give the desired lower concentration.

Example 10.11

Sodium hydroxide solutions are used to neutralize acids, to treat cellulose in the preparation of rayon and to remove potato peels in commercial use. 250 cm^3 of 2M NaOH is mixed with 250 cm^3 of water. Calculate the molarity of resulting solution.

Solution

$$\begin{aligned} 250 \text{ cm}^3 \text{ of } 2\text{M NaOH contain} &= \frac{250 \text{ cm}^3 \times 2}{1000 \text{ cm}^3} \\ &= 0.5 \text{ moles of NaOH} \\ \text{Total volume of solution} &= 250 \text{ cm}^3 + 250 \text{ cm}^3 \\ &= 500 \text{ cm}^3 \\ &= 0.5 \text{ dm}^3 \\ \text{Molarity of resulting solution} &= 0.5 \text{ moles} / 0.5 \text{ dm}^3 \\ &= 1\text{M} \end{aligned}$$

Self Check Exercise 10.5

1. Urea (NH_2CONH_2) is a white solid produced commercially as a fertilizer and starting material for plastics. It is a non-volatile and non-ionizable compound. What is the mole fraction of Urea in an aqueous solution that is 0.25m Urea. (Ans: 4.49×10^{-3})
2. Potassium hydroxide (KOH) is used in the manufacture of liquid soaps, in paints and varnish removers. An experimenter needs 25 cm^3 of 0.015M KOH. What mass of KOH he will dissolve to make this solution. (Ans: 0.021 g)

10.3 RAOULT'S LAW

A French chemist Raoult discovered a quantitative relationship between vapour pressure of solution and concentration of solution. This relationship is known as Raoult's law.

It states that when a nonvolatile solute is dissolved in a solvent, the vapour pressure of solution (P) is directly proportional to the mole fraction of solvent (X_1)

$$P \propto X_1$$

$$\frac{P}{P^0} = X_1 \quad \text{----- (1) where } P^0 \text{ is constant of proportionality and is the vapour pressure of the pure solvent. A more common form of Raoult's law is obtained by simple substitution. In a binary solution } X_1 + X_2 = 1$$

And $X_1 = 1 - X_2$ Where X_2 is mole fraction of solute.

Substituting value of X_1 in equation (1), we get

$$P = P^0 (1 - X_2)$$

$$P = P^0 - P^0 X_2$$

$$P - P^0 = -P^0 X_2$$

$$P^0 - P = P^0 X_2$$

$$\Delta P = P^0 X_2$$

----- (2)

Where $P^0 - P =$ lowering in vapour of solvent (ΔP).

Therefore Raoult's law can also be stated as the lowering in vapour pressure is directly proportional to the mole fraction of solute. Rearranging equation (2) we get another form of Raoult's law.

$$\frac{P^0 - P}{P^0} = X_2$$

$$\frac{\Delta P}{P^0} = X_2$$

$$\frac{P^0 - P}{P^0} \text{ or } \frac{\Delta P}{P^0}$$

is relative lowering in vapour pressure of the solvent. Raoult's law can also be stated as the relative lowering in vapour pressure is equal to the mole fraction of solute. Lowering in vapour pressure depends on temperature whereas relative lowering in vapour pressure is independent of temperature.

Raoult's law for ideal solution of two volatile components (liquids)

Raoult's Law also governs the vapour pressure of mixtures of two or more volatile components. The vapour pressure of each component is determined by its mole fraction and the vapour pressure of the pure component. The total vapour pressure always lies between the vapour pressures of the pure components, and is determined by the mixture composition

Example 10.12

What are the partial pressures of benzene and toluene in a solution in which the mole fraction of benzene is 0.6? What is the total vapour pressure? The vapor pressure of pure benzene is 95.1 mm Hg and the vapour pressure of pure toluene is 28.4 mm Hg at 25°C.

The student should be guided to choose useful information to solve various problems.

Problem Solving Strategy

1. Remember that the sum of mole fractions of all the components of solution is unity.
2. Mole fraction of benzene is given find the mole fraction of toluene on the basis of point 1.
3. Find the partial pressure of each component of solution using formula.
4. Find total pressure by adding the two partial pressures.

Solution

If $X_{\text{benzene}} = 0.6$, then $X_{\text{toluene}} = 0.4$ because $1 - 0.6 = 0.4$.

Now that we know the mole fractions and vapor pressures.

$$P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^0 = (0.6)(95.1 \text{ mm Hg}) = 57.1 \text{ mm Hg}$$

$$P_{\text{toluene}} = X_{\text{toluene}} P_{\text{toluene}}^0 = (0.4)(28.4 \text{ mm Hg}) = 11.4 \text{ mm Hg}$$

The total vapor pressure is simply the sum of the partial pressures:

$$P_{\text{total}} = P_{\text{benzene}} + P_{\text{toluene}} = 57.1 \text{ mm Hg} + 11.4 \text{ mm Hg} = 68.5 \text{ mm Hg}$$

10.3.1 Causes of Lowering in Vapour Pressure

Every liquid has a definite vapour pressure at a particular temperature (see Chap 5). In a pure liquid, all the surface particles are that of the liquid. But in a solution containing a nonvolatile solute, both solute and solvent particles occur on the surface. The solute particles decrease the number of solvent surface particles, (see figure 10.5). Which beaker contains less numbers of solvent particles on the surface? In which beaker solvent will have higher vapour pressure?

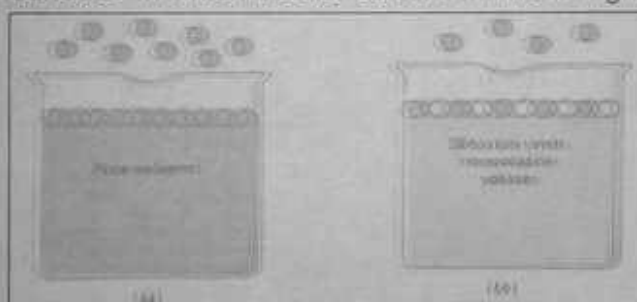


Figure 10.5: lowering of vapour pressure

Decreasing the number of surface solvent particles decreases the rate of evaporation of the solvent, which decreases the vapour pressure. Thus the vapour pressure of a solution containing a nonvolatile solute is always less than the vapour pressure of the pure solvent.

10.4 COLLIGATIVE PROPERTIES OF SOLUTIONS CONTAINING NON-ELECTROLYTE SOLUTES

Have you ever seen salting roads in Muree during snowing? Have you ever added salt to water when cooking pasta? If so, you have already been exposed to a group of four physical phenomena called colligative properties.

In the preceding sections we saw how the presence of solute always lowers the vapour pressures of the solutions. Since a lower vapour pressure implies a higher boiling point, we can also conclude that the presence of nonvolatile solute always raises the boiling point of solvent. It also decreases the freezing point of the solvent. Thus certain properties of solutions depend only on number of solute particles and not on their nature. These properties are called as **colligative properties**. Colligative properties are properties of solutions that depend upon the ratio of the number of solute particles to the number of solvent molecules in a solution, and not on the type of chemical species present. The word colligative means "to collect". Four such related properties are:

- (i) Vapour pressure lowering
- (ii) Boiling point elevation
- (iii) Freezing point depression
- (iv) Osmotic pressure.

The study of colligative properties has provided methods of molecular weight determination.

10.4.1 Lowering of Vapour Pressure

When a non-volatile solute is dissolved in a solvent, the escaping tendency of solvent molecules from the surface of the solution decreases. Thus its vapour pressure is lowered (see section 10.3.1).

According to the Raoult's law relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{\Delta P}{P^0} = X_2$$

If n_1 and n_2 are the number of moles of the solvent and solute respectively, then

$$X_2 = \frac{n_2}{n_1 + n_2}$$

$$\text{So } \frac{\Delta P}{P^0} = \frac{n_2}{n_1 + n_2}$$

Since for dilute solutions $n_2 \ll n_1$, n_2 can be ignored in the denominator

$$\therefore \frac{\Delta P}{P^0} = \frac{n_2}{n_1}$$

If W_1 and W_2 are masses of solvent and solute while M_1 and M_2 are their molecular masses respectively, then

$$n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$$\text{So } \frac{\Delta P}{P^0} = \frac{W_2/M_2}{W_1/M_1}$$

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

$$\text{Or } M_2 = \frac{W_2 \times M_1 \times P^0}{W_1 \times \Delta P}$$

Thus molecular mass of a non-volatile solute can be calculated from this equation.

Example 10.12

When 106.3g of an organic compound M dissolved in 863.5g of benzene, the vapour pressure of benzene is lowered from 98.6 to 86.7 torr. Calculate the molecular mass of M.

Solution

$$P^0 = 98.6 \text{ torr}$$

$$P = 86.7 \text{ torr}$$

$$\Delta P = P^0 - P$$

$$= 98.6 - 86.7$$

$$= 11.9 \text{ torr}$$

$$W_2 = 106.3 \text{ g}$$

$$W_1 = 863.5 \text{ g}$$

$$M_1 = 78 \text{ g/mole}$$

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

$$= \frac{106.3 \text{ g} \times 78 \text{ g/mole} \times 98.6 \text{ torr}}{863.5 \text{ g} \times 11.9 \text{ torr}}$$

$$= 79.56 \text{ g/mole}$$

10.4.1 Causes of Boiling Point Elevation and Freezing Point Depression

A liquid boils at a temperature where its vapour pressure becomes equal to the atmospheric pressure. On the other hand, the freezing point of a substance is the temperature at which liquid and solid phases of a substance co-exist in equilibrium. At this temperature liquid and solid phases of the substance have the same vapour pressure. Solute particles effect both the boiling point and freezing point of a pure solvent. A pure liquid has only one type of particle. But when a non-volatile and non-electrolyte solute is added to a solvent, its vapour pressure is decreased (see section 10.3.1). This is because in solution both solute and solvent particles occur on the surface. Thus solute particles decrease the number of solvent surface particles. This decreases the rate of evaporation of solvent, which decreases the vapour pressure. Therefore, a solution must be heated to a higher temperature than the boiling point of pure solvent to equalize its

The student should be guided to appraise the significance of the information.

vapour pressure to the atmospheric pressure. Thus addition of solute to a pure solvent causes an elevation of the boiling point of solution.

Similarly, decrease in vapour pressure of a pure solvent on the addition of a solute also affects the freezing point of the solution. The solution will freeze at a temperature at which vapour pressure of both solution and solid solvent are the same. This means solution will freeze at a lower temperature than that of the pure solvent. Thus addition of a non-volatile solute also causes a decrease or depression in freezing point of solution.

10.4.2 Quantitative Aspects of Boiling Point Elevation

Experiments have shown that when one mole of non-electrolyte and nonvolatile solute is dissolved in 1 kg of water boiling point is raised 0.52°C . This value is known as the molal boiling point elevation constant (ebullioscopic constant) for water. Figure 10.6 shows how the vapour pressure influences the boiling point. Curve AB represents variation in vapour pressure of pure solvent with temperature. The solvent boils at temperature T_1 when its vapour pressure becomes equal to the external pressure P° . The curve CD represents variation in vapour pressure of solution with temperature. This curve must lie below that of pure solvent. This is because the vapour pressure of solution at all temperatures is lower than that of the pure solvent. The solution will boil at higher temperature T_2 to equalize its vapour pressure to external pressure P° .

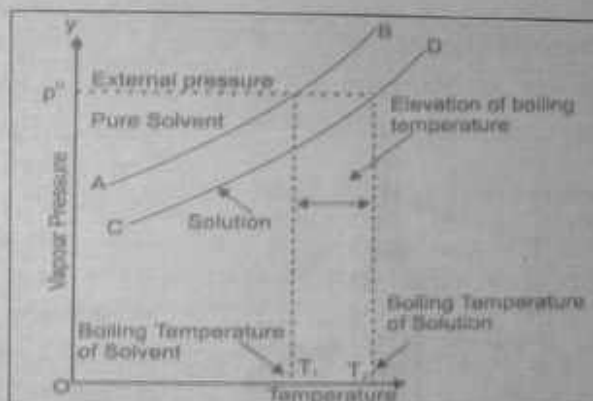


Figure 10.6: Elevation of boiling point – temperature curve

The difference of two boiling points gives the elevation of boiling point (ΔT_b)

$$\Delta T_b = T_1 - T_2$$

The magnitude of the boiling point elevation is directly proportional to the molality of solution,

$$\begin{aligned} \Delta T_b &\propto m \\ \Delta T_b &= \Delta K_b m \quad \dots\dots(1) \end{aligned}$$

The constant K_b is called molal boiling point elevation constant or ebullioscopic constant, or a 1 molal solution.

$$\Delta T_b \propto K_b$$

Thus elevation of boiling point when 1 mole of non-volatile, non-electrolyte solute is dissolved in 1 kg of solvent is called molal boiling point elevation constant. The value of K_b depends only on the nature of the solvent and is independent of nature of solute used. The nature of solute does not effect boiling point of elevation as long as the solute does not ionize.

The student should be guided to use information to solve different data

The molality m of the solution containing W_2 of solute of molecular mass M_2 dissolved in W_1 of the solvent is given by

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

Substituting the value of m in eq(1) we have

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

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

This equation is used to determine the molecular mass of solute.

Self Check Exercise 10.6

Glycerol ($C_3H_8O_3$) is a syrupy, sweet tasting liquid used in cosmetics and candy. It is a non-volatile and non-electrolyte compound. What is the freezing point of an aqueous solution that is 0.25m glycerol? (Ans: 0.465°C)

10.4.3 Measurement of Boiling Point Elevation:

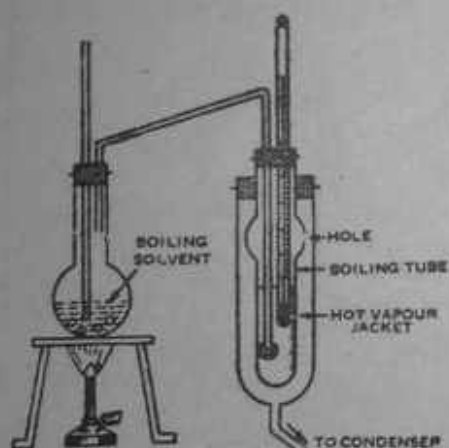


Figure 10.7: Landsberger's apparatus for measurement of elevation of boiling points.

Lands Berger's Method

The apparatus used is shown in Fig 10.7. It consists of four major parts.

- A graduated inner tube with a hole in its side.
- A boiling flask which sends the solvent vapours into the inner tube through a rosehead.
- An outer tube, which receives solvent vapours coming out from the side hole of the inner tube.
- A Beckmann thermometer which can read upto 0.01K

Lands Berger's method can be understood by the following activity.

ACTIVITY:

Cholesterol is an important compound in our body. Its excess has been implicated as a cause of heart disease. Take 100 cm^3 of pure benzene (solvent) in the inner tube. Boil benzene in the boiling flask and pass its vapours through the benzene in the inner flask. These vapours will boil benzene in the inner tube by its latent heat of condensation. Record the temperature at which benzene is boiled in the inner tube. You will observe that benzene will boil at 5.5°C . Now stop the supply of vapours temporarily. Drop 4.5g of cholesterol in the inner tube. Pass vapours of the benzene from boiling flask again to boil the solution. Record boiling point of the solution. Thermometer will show 6.07°C . Now stop the supply of benzene vapours. Remove thermometer and rose head from the inner tube and note the volume of solution. It will be 121.5 cm^3 . Determine density of this solution. Its density will be 0.897 g cm^{-3} . From the volume and density

10. Solution and Colloids

Determine the mass of solution. From the mass of solution determine the mass of benzene. From this data calculate the molecular mass of Cholesterol.

Solution:

Mass of Cholesterol	= $W_2 = 4.5 \text{ g}$
Mass of Benzene	= $W_1 = ?$
Boiling Point of Benzene	= $T_1 = 5.5^\circ\text{C}$
Boiling Point of Solution	= $T_2 = 6.07^\circ\text{C}$
K_b for Benzene	= 5.12
Volume of solution	= $V = 121.5 \text{ cm}^3$
Density of solution	= $d = 0.897 \text{ g cm}^{-3}$
Molecular mass of Cholesterol	= $M_2 = ?$

As,

$$d = \frac{m}{V}$$

$$m = d \times V$$

$$\therefore \text{Mass of Solution} = 0.897 \times 121.5$$

$$= 108.99 \text{ g}$$

$$\text{Mass of Benzene } (W_1) = \text{Mass of solution} - \text{Mass of Cholesterol}$$

$$W_1 = 108.99 - 4.5$$

$$= 104.486 \text{ g}$$

As,

$$\Delta T_b = T_2 - T_1$$

$$\therefore \Delta T_b = 6.07 - 5.5$$

$$= 0.57^\circ\text{C}$$

Now

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

$$= \frac{4.5 \times 5.12 \times 1000}{0.57 \times 104.486}$$

$$= 386.86 \text{ g mole}^{-1}$$

Self Check Exercise 10.7

Calculate the boiling point of a solution containing 12.5g of benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$ in 110g of benzene. Boiling point and K_b of benzene are 80.1°C and 2.53 respectively.

(Ans: 82.637°C)

10.4.4 Quantitative Aspects of Freezing Point Depression

The difference in the freezing points of pure solvent and solution is called the depression of freezing point.

Figure 10.8 shows how the vapour pressure influences the freezing point. Curve ABC is for the pure solvent. The solvent freezes at temperature T_1 corresponding to the point B when its vapour pressure is P° . The portion of the curve BC is for the solid solvent. Greater slope of curve BC indicates a rapid change of vapour pressure with temperature.

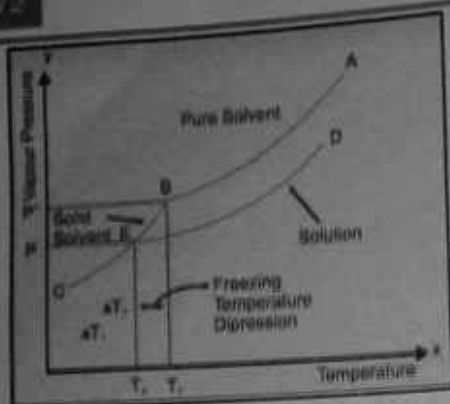


Figure 10.8: Depression of freezing point - temperature curve.

The curve DEC is for the solution. It meets curve BC at point E which is freezing point of solution T_2 when its vapour pressure is P which is lower than P^0 . This is because vapour pressure of solution is always less than that of the pure solvent.

The Difference between the two freezing points gives the depression of the freezing point ΔT_f .

$$\Delta T_f = T_1 - T_2$$

Experimentally $\Delta T_f \propto m$

$$\Delta T_f = K_f m \quad \text{----- (1)}$$

Where K_f is constant called the molal freezing point

constant or the cryoscopic constant. For 1 molal solution.

$$\Delta T_f = K_f$$

Thus the depression of freezing point when 1 mole of non-volatile, non-electrolyte solute is dissolved in 1 kg of solvent is called molal freezing point depression constant.

The value of K_f depends upon the nature of the solvents and is independent of the solute used. The nature of solute does not affect the freezing point depression as long as the solute doesn't ionize.

The molality m of the solution containing W_2 of solute of molecular mass M_2 dissolved in W_1 of the solvent is given by

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

Substituting the value of m in eq (1)

We have

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

Rearranging

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

This equation is used to determine the molecular mass of solute.

10.4.5 Measurement of Freezing Point Depression:

Beckmann's Method

The apparatus used is shown in Fig 10.9. It consists of four parts.

- An inner freezing tube with a side arm. It is fitted with a stirrer.
- An outer tube in which freezing tube is adjusted. This tube serves as air jacket and helps to achieve a slower and more uniform rate of cooling.
- A large vessel containing a freezing mixture.
- A Beckmann thermometer which can read up to 0.01K.

10. Solution and Colloids

Beckmann's method can be understood by the following activity.

ACTIVITY:

In large quantities, the nicotine is a deadly poison. Take 13.4 g of pure water (solvent) in the freezing tube. Now fix thermometer in it, such that the bulb of the thermometer immerse in the solvent. Place freezing tube in the air jacket and air jacket in the large vessel containing a freezing mixture. Record accurate freezing point of solvent. After this remove freezing tube from the air jacket and re-melt the solvent. Add 3.62g of nicotine in the solvent through the side arm. Place freezing tube again in the air jacket and record freezing point of solution while stirring the solution constantly. Thermometer will show -0.563°C . Find the difference of the two freezing points. This will give the value of ΔT_f . From this data determine molecular mass of nicotine.

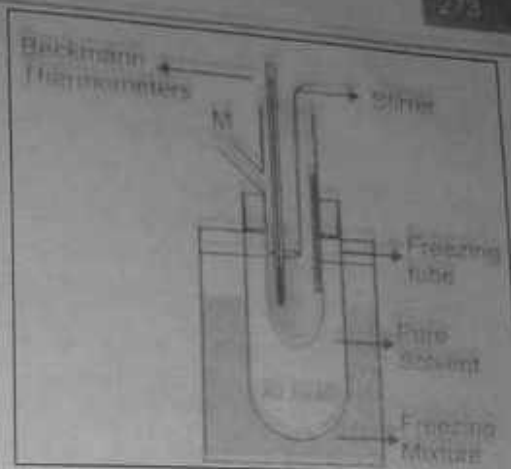


Fig 10.9: Beckmann's apparatus for measurement of depression of freezing point.

Solution

$$\text{Mass of Nicotine} = W_2 = 3.62 \text{ g}$$

$$\text{Mass of water} = W_1 = 73.4 \text{ g}$$

$$K_f \text{ for water} = 1.86$$

$$\text{Freezing point of water} = T_1 = 0^{\circ}\text{C}$$

$$\text{Freezing point of solution} = T_2 = -0.563^{\circ}\text{C}$$

$$\text{Molecular mass of nicotine} = M_2 = ?$$

$$\begin{aligned} \Delta T_f &= T_1 - T_2 \\ &= 0 - (-0.563) \\ &= 0.563^{\circ}\text{C} \end{aligned}$$

Now

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

$$M_2 = \frac{1.86 \times 3.62 \times 1000}{73.4 \times 0.563}$$

$$M_2 = 162.93 \text{ g mole}^{-1}$$

Thus molecular mass of nicotine is $162.93 \text{ g mole}^{-1}$

Self Check Exercise 10.8

1. Vitamin K_1 is a substance found in green leafy vegetables. It is needed by the body to produce a blood-clotting factor. A solution of 55.8 mg of vitamin K_1 in 1.048g of Benzene (freezing point of benzene is 5.455°C) has a freezing point of 4.850°C . K_f for benzene is 5.12. What is the molecular weight of Vitamin K_1 ?

(Ans: $450.596 \text{ g.mole}^{-1}$)

2. Ethylene glycol $C_2H_6O_2$ is added to automobile radiator to prevent cooling water from freezing. Calculate the freezing point of ethylene glycol solution that contains 2kg ethylene glycol dissolved in 5 kg water. ($K_f = 1.86$). Also calculate the boiling point of this solution ($K_b = 0.52$).
(Ans: F.P = -11.99°C , B.P = 103.35°C)

De-icing of aeroplane is based on freezing point depression. Think how?

Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl and CaCl_2 . This is because it depresses the freezing point of the water.

Daily Life Applications of Depression of Freezing Point and Elevation of Boiling Point

Ethylene glycol is used as an antifreeze. It is nonvolatile in character and completely miscible with water. When mixed with water it not only lowers the freezing point but also raises the boiling point. In winter it protects a car by preventing the liquid from freezing whereas in hot summer it protects the radiator from over heating.

The principle of freezing point depression is also used to prepare a freezing mixture for use in an ice cream machine. For this purpose NaCl or NaNO_3 is used to lower melting point of ice.

10.4.6 Osmotic Pressure

You should not drink seawater, if you are stranded in an ocean. Sea water has higher osmotic pressure than most of the fluids in your body. If you drink it, will pull water out of your body cells. Your cells will die of thirst and you will also die.

Osmotic pressure is the pressure which needs to be applied to a solution to prevent the inward flow of water across a semipermeable membrane. It is also defined as the minimum pressure needed to nullify osmosis.

The osmotic pressure of an ideal solution with low concentration can be approximated using the Morse equation (named after Harmon Northrop Morse).

Movement of water molecules from higher concentration to the lower concentration through semi-permeable membrane.

$$\pi = MRT$$

Where

π is osmotic pressure

M is the molarity

$R = 0.08205746 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ is the gas constant

T is the thermodynamic (absolute) temperature

Certain animal membranes such as that of bladder or outer covering of intestines are semipermeable. They allow the passage of

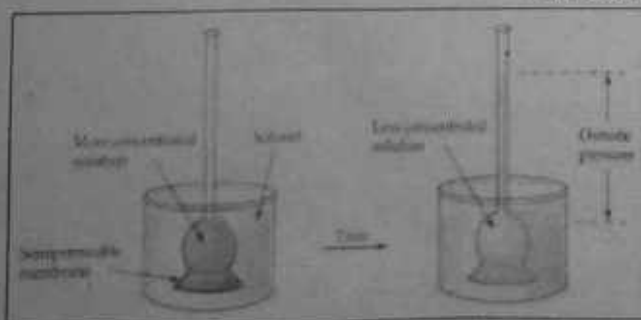


Figure 10.10: The phenomenon of osmosis

The student should be guided to interpret information.

but not any solute dissolved in the water. A man made material such as cellophane can be used as semipermeable membrane.

A solution inside the bulb is separated from pure solvent in the beaker by a semipermeable membrane as shown in figure 10.10.

As time passes the volume of solution increases and that of solvent decreases. The process continues until the hydrostatic pressure due to the extra height of the solution prevents further osmosis. Therefore the osmotic pressure of a solution is defined as the pressure, which must be applied above the solution to prevent passage of solvent through a semipermeable membrane into the solution.

Most important applications of osmosis are found in living organisms. If red blood cells are placed in pure water, the cells expand and ultimately rupture as a result of water entering the cells through osmosis. The osmotic pressure of the fluid inside the cell is equivalent to that of 0.95% NaCl solution. Thus if cells are placed in 0.95% solution of NaCl, there is no net flow of water through the cell walls and the cell remain stable, this solution is said to be isotonic. Solutions having same osmotic pressures are called isotonic solution. If concentration of NaCl solution is greater than 0.95%, water flows out of the cell walls and the cell shrinks. This NaCl solution is hypertonic. If concentration of NaCl solution is less than 0.95%, water flows into the cell and the solution is called hypotonic.

Daily Life Applications of Osmosis

The osmosis phenomenon manifests itself in many interesting daily life applications.

Biochemists use a technique called haemolysis to study the contents of red blood cells.

These cells are protected from the external environment by a semi permeable membrane.

Red blood cells are placed in a hypotonic solution. Since hypotonic solution is less concentrated than the interior of the cell, water moves into the cells. The cells swell and eventually bursts releasing haemoglobin and other molecules.

2. Osmosis is the major mechanism for transporting water upward in plants. Because leaves constantly lose water to the air by a process called transpiration. As a result, leaf fluids become more concentrated than the ground water. Thus water enters membranes in the roots and rises into the tree. It can create an osmotic pressure that can exceed 20 atm in the tallest trees.

3. A large quantity of sugar is essential to preserve jam and jelly. This is because the sugar helps to kill bacteria that may cause botulism. When a bacterial cell is in a hypertonic solution. The intracellular water tends to move out of the bacterial cell to the more concentrated sugar solution by osmosis. This causes the bacterial cell to shrink and eventually to cease functioning.

4. Food is preserved by coating with salt, which produces hypertonic solution. Thus food coated with salt causes microbes on the surface to shrivel and die from loss of cell water.

14.7 Reverse Osmosis

If a solution in contact with pure solvent across a semipermeable membrane is subjected to an external pressure equal to osmotic pressure, it stops osmosis. If external pressure is

greater than solution's osmotic pressure, it will force solvent to flow from solution to the solvent. This process is called reverse osmosis.

Daily Life Application of Reverse Osmosis

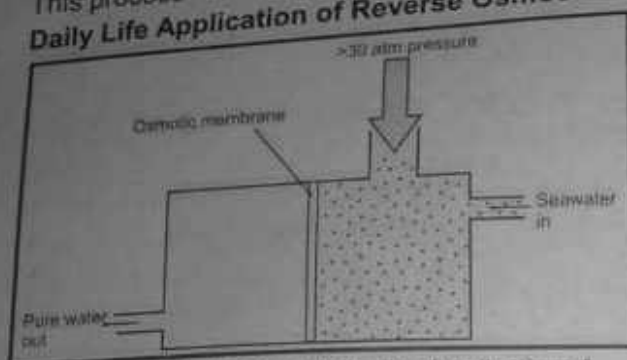


Figure 10.11: A schematic for the desalination of seawater by reverse osmosis

Sea water is highly hypertonic to body fluids and thus is not drinkable. By reverse osmosis it is subjected to desalination (removal of dissolved salts) to make it drinkable. Desalination plant (as shown in figure 10.11), remove large amounts of dissolved salts from sea water. The sea water is pumped under high pressure (20 atm) through the semipermeable membrane, which allow water molecules to pass and stop ions.

Self Check Exercise 10.9

Rank the following aqueous solutions:

- | | |
|---------------------|--|
| i) 0.02m urea | ii) 0.02m glucose in order of decreasing |
| (a) boiling point | (b) freezing point |
| (c) vapour pressure | (d) osmotic pressure |

Colloidal Particles
Dispersed phase = Solute
Dispersion medium = Solvent

10.5 COLLOIDS

Colloids play a very significant role in nature and our life. For instance medicines in colloidal form are easily adsorbed by body tissues and hence are more effective. Do you think milk is a homogeneous mixture?

A heterogeneous mixture of tiny particles of a substance dispersed through a medium is called colloidal dispersion or a colloid. The particles are called colloidal particles or the dispersed phase and the medium is called the dispersion medium or continuous phase (solvent). In a colloid dispersed phase is like solute in a true solution and dispersion medium corresponds to the solvent in the true solution. The dispersed or suspended particles are single large molecules or aggregates of molecules or ions ranging in size from 1 to 10^3 nm. This means these particles are bigger in size than those of true solutions. These particles are visible in electron microscope but invisible in ordinary microscope. For example, Milk, mayonnaise, smoke, rubber, foam, soap, fog, mist, gem stones like black diamond, opal etc.

When a protein crystal is dropped into water, the polymer molecules dissolve to produce a colloidal dispersion. Such colloidal dispersions in which dispersed phase shows an affinity of attraction for the dispersion medium are called lyophilic (means solvent loving). The molecules of dispersed phase are called **lyophilic molecules**. Examples of lyophilic colloids are proteins, gum, gelatin, starch etc in water.

When solid AgCl is brought in contact with water, it does not spontaneously disperse to form a colloid. Such a colloid, which cannot be made by spontaneous dispersion is called

lyophobic (means solvent hating). The molecules of dispersed phase of such colloids have very little or no attraction for the dispersion medium, are called **lyophobic molecules or particles**. Examples of lyophobic colloids are sulphur, gold, Iron (III) hydroxide in water.

10.5.1 Suspensions

Mix one tea spoon full of sand or mud in a glass of water. What happens? Leave it undisturbed for some time. What happens?

A dispersions in which particles of the dispersed substance are visible to the naked eye are called suspensions. Sizes of these particles are greater than 10^3 nm. This means these particles are bigger than these of colloids. These particles cannot pass through ordinary filter paper. They settle down under the influence of gravity. Suspensions scatter and reflect light. For example, Mud or sand in water are suspensions.



Science Tithi

Blue colour of sky is due to the scattering of light by colloidal dust particles in air. Similarly sea water looks blue due to scattering effect of light by the colloidal impurities in sea water.

10.5.2 Properties of Colloids

General properties of colloids are as follows:

1. Most colloids are cloudy or opaque, but some are transparent to the naked eye
2. When light passes through a colloid, it is scattered by the dispersed particles because their sizes are similar to the wavelength of visible light. When viewed from the side, the scattered beam is visible and broader than that one passing through a solution. This phenomenon is known as Tyndall effect (see Fig 10.12).
3. Colloidal particles exhibit Brownian motion. This can be seen under low magnification. This is because colloidal particles are pushed this way and that way by molecules of dispersing medium.
4. Colloidal particles do not coagulate into larger particles and settle out. This is due to the fact that particles have charged surfaces. These surfaces interact with the molecules of dispersing medium. For example, aqueous protein has charge amino acid groups facing the water and uncharged groups buried within the molecule.



Figure 10.12: Light scattering by colloidal suspensions

5. Temperature changes affect colloids. Increase in temperature makes the colloidal particles move faster and colloid more often and convert little particles into a lump. This means increase in temperature causes coagulation. For example, heating milk causes coagulation of casein in milk.

6. Colloidal particles have little power of diffusion. This is because the colloidal particles have very large size as compare to ordinary solute particles (see table 10.4).
7. Colloidal particles can pass through ordinary filter paper but cannot pass through ultra filter papers.
8. Colloidal particles have high ratio of surface area to volume as compared to the particles of true solutions.
9. Colloidal particles do not settle under the influence of gravity.

10.5.3 Types of Colloids

Colloids are classified according to whether the dispersed and dispersing substances are gases, liquids or solids. Table 10.3 lists some common types of colloids and their examples.

10.3 Types of colloids

Colloid Type (Common Name)	Nature and Composition	Example
Sol	Solid particles dispersed through a liquid	Milk of magnesia, starch dispersed in water, paints, coloured glasses, gems
Gel	Continuous network of solid through out the liquid medium	Halwa, jellies, gelatin
Aerosol	Either a solid or a liquid dispersed in a gas	Smoke (solid expressed in air), fog (liquid dispersed in air)
Emulsion	Liquid dispersed in an another liquid	Milk, mayonnaise
Foam	Bubbles of a gas suspended in a liquid or a solid	Canned shaving cream, soap leather, whipped cream

10.5.4 Comparison of Colloids, Suspensions and True Solutions

The properties of a colloid depend mainly on the size, shape and charge of dispersed particles. Table 10.4 shows, some of the distinctive properties of colloids, suspensions and true solutions.

Table 10.4: Some properties of colloids, suspensions and true solutions

Sr. No.	Properties	Colloids	Suspensions	True solutions
1.	Size of particles	$1-10^3$ nm	$> 10^3$ nm	$0.1 - 1$ nm
2.	Phase	Heterogeneous	Heterogeneous	Homogenous
3.	Aggregates	Particles are composed of 10^3 to 10^9 atoms	Particles are composed of more than 10^9 atoms	Particles are composed of 1 to 10^3 atoms
4.	Charge on the particles	Positive or negative	Positive or negative or may be neutral	Both positive and negative or may be neutral
5.	Visibility of particles	Invisible by naked eye and ordinary microscope but visible in electron microscope	Visible by the naked eye and in ordinary microscope	Indivisible by the naked eye, ordinary microscope as well as electron microscope
6.	Filterability	Particles can pass through ordinary filter paper, but cannot pass through ultra filter paper	Particles cannot pass through ordinary as well as ultra filter paper.	Particles can pass through ordinary as well as ultra filter paper.
7.	Dispersion of light	Scatter light	Scatter light	Cannot scatter light
8.	Effect of gravity	Particles do not settle under the influence of gravity	Particles settle under the influence of gravity	Particles do not settle under the influence of gravity

Summary of the Key Terms

1. A solution is a homogenous mixture of two or more substances, which may be solids, liquids or gases. The solubility of a solute in a given solvent depends on the interactions between the solute and the solvent particles. Substances that have similarly intermolecular forces tend to dissolve in each other, leading to the generalization "like dissolves like".
2. A rise in temperature usually increases the solubility of solids and liquids but decrease the solubility of gases.

3. Raoult's Law states that when a non-volatile solute is dissolved in a solvent, the vapour pressure of the solution (P) is directly proportional to the mole fraction of the solvent (X_1)

$$P = P^0 X_1$$
4. The concentration of a solution can be expressed as percent by mass, percent by volume, molarity, molality, mole fraction, ppm, ppb and ppt. The unit of concentration most commonly used by the chemist is molarity, which is defined as the number of moles of solute dissolved per dm^3 of solution.
5. Sometimes it is useful to know the ratio of the amount of solute to the amount of solvent. For this purpose units of molality and mole fraction are used. These units are particularly important in the study of colligative properties that depend only on the number of solute particles that are present and not on their nature.
6. Vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are colligative properties of solution. Adding a solute to a solvent lowers the vapour pressure of the solvent. This causes an elevation in boiling point and depression in freezing point of solution.
7. Osmotic pressure causes the solvent to flow across a semi-permeable membrane when the concentrations of solute on either side of the membrane are unequal.
8. Colligative properties can be used to determine the molecular weight of the solute. This is because these properties depend only on the number of solute particles in a solution and not on their identity.
9. Sea water can be made drinkable by the process of reverse osmosis.
10. A colloid is a heterogeneous mixture of tiny particles of a substance dispersed through a medium. These particles are only visible in electron microscope. When light passes through a colloid, it is scattered by the dispersed particles. This phenomenon is known as Tyndall effect.
11. A dispersion in which particles of the dispersed substance are visible to the naked eye is called suspensions.

References for additional information:

- Silberberg, Chemistry the Molecular Nature of Matter and Energy
- Olmsted and Williams, Chemistry, the Molecular Science
- Zumdahl, Introductory Chemistry
- Raymond Chang, Essential Chemistry
- Caret, Demniston, Topping, Principles and Applications of Inorganic, Organic and Biological Chemistry



Exercise

1: Choose the correct answer

- (i) 18g glucose is dissolved in 180g of water. The relative lowering of vapour pressure is
 (a) 1 (b) 1.8 (c) 0.01 (d) 0.001
- (ii) 100g of a 10% (W/W) NaOH contains 10g of NaOH in

10. Solution and Colloids

281

- (a) 100g of H_2O (b) 110g of H_2O (c) 10g of H_2O (d) 100g solution.
- (iii) Which of the following W/W solutions has the lowest freezing point?
 (a) 18% glucose (b) 6% urea (c) 34.2% sucrose (d) 9% glucose
- (iv) All solutions containing 1g of non-volatile solutes will have
 (a) Same vapour pressure (b) Same boiling point
 (c) Same freezing point (d) all of a, b, c.
- (v) Molarity of pure water is
 (a) 1 (b) 1.8 (c) 55.5 (d) 18
- (vi) A solution of urea (Mol.Wt=60) is 10% (W/V). the volume in which 1 mole of it is dissolved will be.
 (a) 6 dm³ (b) 0.6 dm³ (c) 60 cm³ (d) 0.54 dm³
- (vii) The solubility of a substance decreases with increase in temperature if heat of solution is
 (a) positive (b) negative
 (c) zero (d) cannot be predicted
- (viii) Molarity of glucose solution when 9g of it is dissolved in 250 cm³ of solution is
 (a) 0.25M (b) 0.2m (c) 0.5M (d) None of these
- (ix) Sea water has about 6 ppm dissolved oxygen. What mass of dissolved oxygen is present in one kg of sea water.
 (a) 6g (b) 6×10^{-3} kg (c) 6×10^{-3} g (d) 6×10^{-3} mg
- (x) Which of the following is volatile
 (a) glucose (b) urea (c) sucrose (d) water
- (xi) Which of the following is not true of a colloid.
 (a) it is heterogeneous (b) scatter light
 (c) can pass through ultra filter paper
 (d) Its particles cannot be seen under ordinary microscope.
- (xii) Aerosol are colloids which contain
 (a) A solid dispersed in a liquid (b) A solid dispersed in a gas
 (c) A liquid dispersed in a gas (d) A liquid in another liquid
1. a 2. a, b 3. b, c 4. c, d

2. Determine the molality of the following solutions

i) 3.5% (W/W) glucose (aq)

(Ans: 0.2 m)

ii) 9.9g $NaNO_3$ dissolved in 940g of water

(Ans: 0.124 m)

3. What are the freezing and boiling points of a solution prepared by dissolving 13.3g ethylene glycol in 100g of water.

(Ans: F.P = -3.99°C, B.P = 101.115°C)

4. When cooking, what effect does adding salt to water have on the time required to boil food?

5: Concentrated sulphuric acid is 98% (W/W) H_2SO_4 (aq). Its density is $1.84\text{g}\cdot\text{cm}^{-3}$. Calculate

i) The molarity of the solution

(Ans: 18.4 M)

ii) The molality of the solution

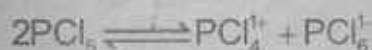
(Ans: 10 molal)

iii) What quantity of conc. H_2SO_4 is required to prepare 500cm^3 of 0.1M H_2SO_4 .

(Ans: 2.717cm^3)

6. What would you expect potassium chloride, KCl, an ionic solid to be more soluble in H_2O or CCl_4 ? Explain your prediction.
7. List three factors that accelerate the dissolution process.
8. Explain the nature of solutions in liquid phase giving examples of completely miscible, partially miscible and immiscible liquid-liquid solutions.
9. Express solution concentration in terms of mass percent, molality, molarity, parts per million, parts per billion and parts per trillion and mole fraction.
10. Distinguish between the solvation of ionic species and molecular substances.
11. Describe the role of solvation in the dissolving process.
12. Define the term water of hydration.
13. Define the term colligative.
14. List the characteristic of colloids and suspensions.
15. Define hydrophilic and hydrophobic molecules.
16. Describe on a particle basis why a solution has a lower vapour pressure than the pure solvent.
17. Explain osmotic pressure, reverse osmosis and give their daily life applications.
18. Define heat of solution and apply this concept to the hydration of ammonium nitrate crystals.
19. Interpret the phenomenon of freezing in a mixture of ice and salt.
20. Interpret how solute particles may alter the colligative properties.
21. Interpret the effect of temperature on solubility.
22. Compare molal and molar solutions.
23. Explain the following
 - (a) Molality is independent of temperature but molarity depends on it.
 - (b) One molal solution of glucose in water is dilute as compared to one molar solution of glucose, but the number of particles of solute is the same.
 - (c) The total volume of solution by mixing 50cm^3 of ethanol and 50cm^3 of water may not be equal to 100cm^3 , why?
 - (d) NaCl and NaNO_3 are used to lower the melting point of ice.
 - (e) In summer the antifreeze solutions protect the radiator from boiling over.

- (f) One molal and two molal solutions of urea boil at different temperatures.
 (g) Relative lowering of vapour pressure is independent of the temperature.
 (h) The sum of mole fractions of all the components is always equal to one.
24. 1.89g of an organic compound, A was dissolved per 85cm³ of water (d=0.998g cm⁻³). The boiling point under one atmospheric pressure of this solution is increased to 100.106°C. What is the molecular weight of A.
 (Ans: 109.2978.4)
25. What freezing point do you expect for water in which 17.9g sucrose C₁₂H₂₂O₁₁ is dissolved per 47.6g of H₂O.
 (Ans: -2°C)
26. The vapour pressure of pure water is 23.756 torr at 25°C. How much glucose would be added to 100g of water to bring the vapour pressure down to 23.00 torr? (Ans: 31.82g)
27. You are provided 98%(W/W) H₂SO₄ having density 1.84 gcm⁻³. How much volume of this H₂SO₄ is required to obtain one dm³ of 30% (W/W) H₂SO₄ which has density 1.25g cm⁻³. This solution is used in lead storage batteries as electrolyte.
28. Caffeine is about 10 times more soluble in hot water than in cold water. Is $\Delta H^\circ_{\text{sol}}$ of caffeine in water is positive or negative?
29. PCl₅ can react with itself in a reversible reaction to form a salt that contains the PCl₄⁺ and PCl₆⁻ ions.



The extent to which this reaction occurs depends on the solvent in which it is run. Predict whether a non polar solvent such as CCl₄ favours the product or the reactants of this reaction. Predict what would happen to this reaction if we use a polar solvent.

(Ans: -8.5°C)

30. An aqueous solution of a compound boil at 102.4 °C. At what temperature will this solution freeze?
 (Ans: 8.5 85 °C)
31. Water and carbon tetrachloride are not miscible. When mixed they form two layers. If an aqueous solution of iodine I₂ is shaken with CCl₄, the iodine is extracted into the CCl₄ layer. Interpret this behavior on the basis of your knowledge of intermolecular forces.
32. A Cucumber placed in concentrated brine (concentrated NaCl solution in water) shrivels into a pickle. Give argument to support this observation?
33. Two beakers are placed in a sealed bell jar. One beaker contains water and the other contained concentrated glucose solution. With time volume of water decreases and solution volume increases. Suggest reason?
34. Consider two aqueous solutions one is sucrose and the other of glucose. Both of these solutions boil at 101.52 °C. List some common properties of these solutions.
35. Design an experiment to determine water of crystallization in a compound.



THERMOCHEMISTRY



After completing this lesson, you will be able to:

- Define thermodynamics.
- Define the terms system, surrounding, boundary, state function, heat, heat capacity, internal energy, work done and enthalpy of a substance.
- Name and define the units of thermal energy.
- Define bond dissociation energy.
- Classify reaction as exothermic or endothermic.
- Apply Hess's Law to construct simple energy cycles.
- Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure.
- Use the experimental data to calculate the heat of reaction using a calorimeter.
- Specify conditions for the standard heat of reaction.
- Explain reaction pathway diagram in terms of enthalpy changes of the reaction. (Born Haber's Cycle).
- Describe how heat of combustion can be used to estimate the energy available from foods.



Reading

INTRODUCTION

Every process in this universe whether it occurs in living cells, or in test tubes, or in the atmosphere or in water etc. is accompanied by an energy change. Some processes release energy, other require energy. However, in all these cases total amount of energy in the universe remains constant. The branch of thermodynamics that examines the heat involved in chemical reactions is called **thermochemistry**. In this chapter we will discuss the principles that govern energy changes. We will examine the role of energy in chemical reactions. We will also

discuss how heat of a chemical reaction is measured in order to focus on the central topic of the chapter i.e., the amount of heat released or absorbed in a reaction. **The study of all types of energy changes associated with physical and chemical changes is known as thermodynamics.**

11.1 ENERGY IN CHEMICAL REACTIONS

When you burn a fuel such as Sui gas, LPG, wood or oil, energy is released, where this energy comes from?

The energy in the form of heat is either evolved or absorbed as a result of chemical reaction. This is because, in a chemical reaction old bonds are broken and new bonds are formed. Bond breaking always consumes energy and bond making always releases energy. When the energy released by bond forming is greater than the energy consumed by bond breaking, there is a net release of chemical energy. Whereas energy is absorbed, when the

11.1.3 System and Surroundings

The part of the universe on which we wish to focus our attention is called a system. The remaining part of the universe is called surroundings. The real or imaginary surface separating the system from its surroundings is called the boundary.

A system in chemistry is usually the substance undergoing physical or chemical change.

For example, in the study of reaction between limestone and hydrochloric acid solution in a test tube, limestone and hydrochloric acid solution form a system. The test tube and everything around the test tube is surroundings. Similarly in the study of thermal decomposition of a compound, the sample of the compound would be the system. Whereas the beaker, the source of heat and everything else would be surroundings.

11.1.4 Thermochemical Reactions

When a chemical change takes place, energy is exchanged between system and its surroundings. Energy has many forms such as heat, light, work etc. A chemical reaction which proceeds with the evolution or absorption of heat is called a thermochemical reaction. A **balanced chemical equation** which also shows heat change of a chemical reaction is called **thermochemical equation**. The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.

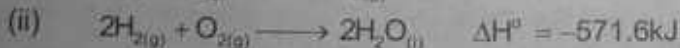
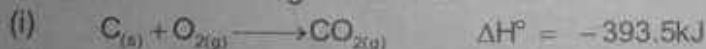
Which of the following chemical equations is a thermochemical equation?



There are two types of thermochemical reactions: -

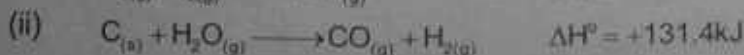
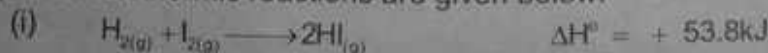
(1) Exothermic Reactions

A chemical reaction that proceeds with the evolution of heat is called an **exothermic reaction**. In an exothermic reaction the chemical system transfers energy to the surroundings as the reactants are converted to products e.g. burning of fuels is a highly exothermic reaction. The energy released can be used to heat a room, or to drive an engine or to cook food. Examples of exothermic reactions are given below:



(2) Endothermic Reactions:

A chemical reaction that proceeds with the absorption of heat is called an **endothermic reaction**. In these reactions heat is transferred from surrounding to the system. Examples of exothermic reactions are given below:



The student should be guided to differentiate between the different parts of the topic

11. Thermochemistry



$$\Delta H^\circ = +180.5 \text{ kJ}$$

287

Self Check Exercise 11.1

- Classify the following processes as exothermic or endothermic.
- (a) Freezing of water
 - (b) Combustion of methane
 - (c) Sublimation of dry ice
 - (d) $H_2O_{(g)} \longrightarrow H_2O_{(l)}$
 - (e) decomposition of limestone.

11.1.4 Heat of Reaction

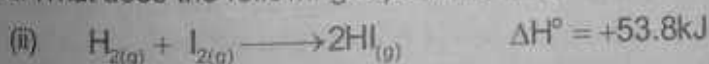
The amount of energy released or absorbed depends on the amount of substances that react. For example, as more fuel burns, more energy is released. Thus when we report an energy change we must also report the amounts of the chemical substances that generate the energy change. For this purpose energy changes are expressed in terms of molar quantities of reactants and products.

The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.

Heat of reaction measured at 25°C (or 298K) and one atmospheric pressure is known as enthalpy change. It is denoted by ΔH° . (for detail see section 11.5.1)

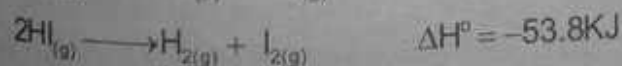
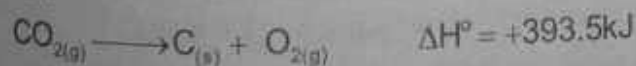


This equation shows that 1 mole of solid carbon (12g) reacts with 1 mole of oxygen gas (32g) to give 1 mole of CO_2 gas (44g) at 25°C and 1 atmospheric pressure and 393.5 KJ heat is evolved. What does the following equation show?



If a reaction is exothermic when going in one direction, it will be endothermic in the reverse direction. When a reaction is reversed, the magnitude of ΔH° remains the same but its sign changes.

Thus above two thermochemical reactions in the reverse direction would be represented as follows:



Do You Know

Chemical reactions support our lives and assist us at home and at work. For instance cellular respiration is a series of chemical reactions that releases energy from the food we eat to "Power" all the functions and activities inside our body. Combustion reactions help release energy to heat our homes and move our vehicles.

The student should be guided to recall information.

When gasoline burns in an automobile engine energy is released. A part of this energy is converted into heat which heats up the engine. The rest of the energy moves piston which turns a crankshaft and the crankshaft does work to move the automobile. Thus chemical energy released when gasoline burns is converted into heat and work. Chemical and related industries manufacture products that release, absorb or retain energy. Fertilizers help growing crops absorb solar energy and convert it into the chemical energy of food. Batteries produce electric energy from chemical reaction (we will discuss it in chapter 12). Thus the transformation of the energy from one form to another is an important field of science called thermodynamics.

The study of all types of energy changes associated with chemical and physical changes is known as thermodynamics.

11.2.1 State Function

A complete description of a system, which includes its quantity, temperature, pressure and volume describe the state of the system.

There are three types of systems, open system, closed system and isolated system.

In an open system reactants and energy may be exchanged with its surroundings. In a closed system only energy may be exchanged with surroundings but not material. Whereas in an isolated system no energy and no material may be exchanged with its surroundings. In fact there is no ideally isolated system. It is hypothetical system used for a comparison.

The condition of a system when various properties like temperature, pressure, volume, number of moles etc of system have definite values is called state of the system. The initial state of a system is its state before it undergoes a change. Whereas the final state is its state after the change has occurred. In a chemical reaction, the description of the products defines the final state.

Variables such as pressure, temperature, volume and energy depend only on the state of the system. A change in any of these variables depends only on the difference between initial and final conditions, but does not depend on the path followed. Such variables are called state functions or state variables.

The properties that are determined by the state of the system regardless of how that condition was achieved are called state functions.

Change in any property of a system is determined by the difference in the value of that property in the final state and the value of the same property in the initial state.

For example

Let V_1 is the initial volume of H_2 gas confined in a cylinder at temperature T_1 , and pressure P_1 . When temperature is increased from T_1 to T_2 , its volume becomes V_2 and pressure changes to P_2 . The changes in volume (ΔV) is given by the following equation,

$$\Delta V = V_2 - V_1$$

Similarly change in temperature ΔT and change in pressure ΔP are given by the equations,

$$\Delta T = T_2 - T_1$$

$$\Delta P = P_2 - P_1$$

Spontaneous and non-spontaneous reactions:

The reactions which proceed on their own and do not need any external energy to proceed are called spontaneous reactions. For example emission of rays from radioactive elements, burning of methane and coal. On the other hand the reactions which require external energy to proceed are called non-spontaneous reactions. For example reaction of nitrogen and oxygen to make nitric oxide, thermal decomposition of P_2O_5 , etc.

11.3 INTERNAL ENERGY

In every chemical process energy is transformed from one form to another. The amount of energy transformed depends upon the energy contents of reactants and products. Every system has definite amount of energy present in it. This energy is due to kinetic as well as potential energies of the particles present in the system. The kinetic energy of the particles is due to the translational, rotational and vibrational motions of particles. The potential energy is due to all types of attractive forces present between the particles. These attractive forces include all types of bonds and Van der Waal's forces. **The sum of all kinds of energies of the particles of the system is called as internal energy.** It is denoted by E . Absolute value of internal energy of a system cannot be measured. However change in internal energy (ΔE) of a system can be measured. The internal energy is a state function and depends only on the initial and final states of the system. Thus:

$$\Delta E = E_2 - E_1$$

where E_1 and E_2 are internal energies in the initial and final states of the system respectively.

11.4 FIRST LAW OF THERMODYNAMICS

A system can exchange energy with its surroundings in two distinct ways. Energy can be transferred as heat or work. Heat and work can be transferred into or out of the system. Because energy must be conserved, the energy change of the system is linked to the flow of heat and work.

$$\Delta E = q + w$$

This equation is the mathematical form of first law of thermodynamics. Where ΔE represents the change in the system's internal energy, q represents heat and w represents work. w has positive sign when work is done on the system and negative when work is done by the system. q is positive when system absorbs heat and negative when loses heat.

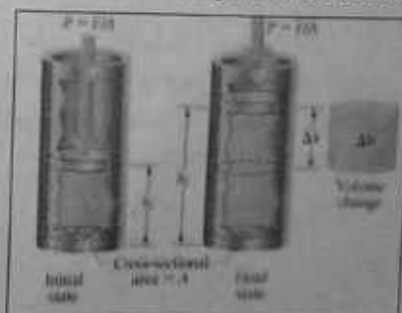


Figure. 11.1: Pressure – volume work

The student should be guided to interpret the information.

Consider a gas confined to a cylinder having a movable piston as shown in Fig. 11.1.

Suppose system absorbs ΔE energy from a source. On absorbing energy gas expands inside the cylinder and pushes the piston through a distance Δh . A part of ΔE absorbed becomes thermal energy q and remaining energy is consumed in doing work w on the piston. Therefore,

$$\Delta E = q + w$$

Since pressure is defined as force per unit area, the pressure of the gas (P) is:

$$P = \frac{F}{A}$$

$$F = P \times A \text{ ----- (1)}$$

Work done on the piston is:

$$\text{Work} = \text{force} \times \text{distance}$$

$$W = F \times \Delta h \text{ ----- (2)}$$

From equations 1 and 2, we get.

$$W = P \times A \times \Delta h \text{ ----- (3)}$$

During expansion, the gas changes its volume. This volume change ΔV is equal to the product of area (A) and displacement (Δh).

$$\Delta V = A \cdot \Delta h$$

Therefore equation 3 becomes.

$$W = P \times \Delta V$$

The gas (the system) is expanding, pushing back the piston against the pressure. Therefore, the system is doing work on the surroundings, so the sign of work should be negative.

$$W = - P \Delta V$$

Such type of work is done in an automobile engine. Heat from the combustion of the fuel expands the gases in the cylinder to push back the piston. The piston turns a crankshaft which does work to move the automobile. This type of work is called as pressure-volume work. Under these conditions:

$$\Delta E = q - P \Delta V$$

11.4.1 Relationship between Internal Energy of a System and Thermal Energy at Constant Temperature and Pressure

Chemical reactions are generally carried out in open containers. Therefore, these reactions take place at constant pressure. This means that volume of reaction mixture can change. Thus, PV work can be done and heat can flow to or from the system. According to the first law of thermodynamics,

$$\Delta E = q_p + P \Delta V$$

Where q_p is the heat transferred to the system from the surroundings. $P \Delta V$ is work done by the surrounding on the system at constant pressure. If the system does work on the surrounding then,

$$\Delta E = q_p - P \Delta V$$



The student must be guided to employ this knowledge to illustrate the information.

Rearranging this equation,

$$q_p = \Delta E + P\Delta V$$

If a chemical reaction involves only PV work at constant pressure, q_p becomes an important quantity. In this case, q_p represents the heat absorbed or evolved by the reaction at constant pressure and is known as enthalpy change, ΔH . Thus, the thermal energy for a reaction is equal to change in internal energy (ΔE) of the system plus PV work done by the system at constant pressure. This thermal energy change is called enthalpy change (ΔH) of the system. Therefore,

$$q_p = \Delta H = \Delta E + P\Delta V \dots\dots\dots(1)$$

Thus, enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume ($H = E + PV$). Absolute value of enthalpy of a system cannot be measured. However, change in enthalpy of a system (ΔH) can be measured.

Since enthalpy change (ΔH) for a reaction is measured as thermal energy or heat (q_p), therefore it is also known as heat of reaction. For a combustion reaction, ΔH is also called as heat of combustion. *Solids & Liquid:-*

Since, there is no appreciable volume change in reactions involving solids or liquids, so $\Delta V = 0$. Therefore, equation (1) becomes,

$$\Delta H = \Delta E + P(0)$$

$$\text{Thus } \Delta H = \Delta E$$

Standard enthalpy change is enthalpy change at constant pressure (1 atm) and constant temperature (25°C) and is denoted by ΔH° . Superscript zero indicates that the reaction has been carried out under standard conditions. Under these conditions reactants and products are in their standard states. (For detail see section 11.5)

Equation (1) can be written as

$$q_p = \Delta H^\circ = \Delta E^\circ + P\Delta V$$

Thus thermal energy change for a reaction is equal to the change in the internal energy of a system plus PV work done by the system at constant temperature and pressure.

11.4.2 Relation between Enthalpy Change and Heat of Reaction or Heat of Combustion of A Reaction

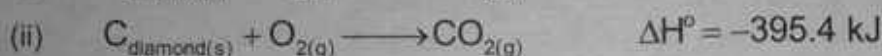
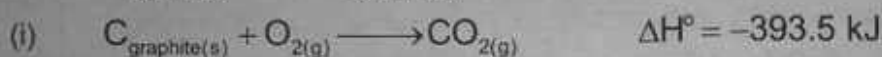
Because most chemical reactions occur at constant pressure, we can equate the heat change in these reactions to the change in enthalpy. This means we can define heat of a reaction as the change in enthalpy (ΔH), as the difference between the enthalpies of the products (final state) and the enthalpies of the reactants (initial state).

$$\Delta H = H_{\text{products}}^{\text{final}} - H_{\text{reactants}}^{\text{initial}}$$

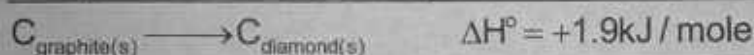
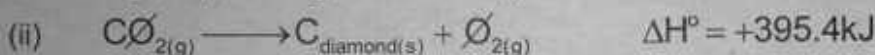
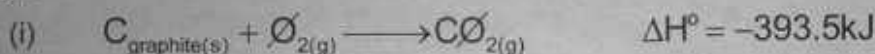
The enthalpy change of a reaction can be positive or negative depending upon the process. For an exothermic process, in which heat is released by the system of the surrounding ΔH is negative (see examples in section 11.1.4). For an endothermic process, in which heat is absorbed by the system from the surroundings ΔH is positive (see examples in section 11.1.4). Since, combustion is an exothermic process in which heat is released by the system to its surroundings, ΔH is negative (see examples in section 11.5).

11.5 STANDARD STATES AND STANDARD ENTHALPY CHANGES

We can measure enthalpy change for a chemical reaction at constant pressure using a calorimeter. However, it is not only very difficult but also impossible in many cases. This is because some reactions are too slow. For example value of ΔH for the conversion of graphite to diamond cannot be measured in a calorimeter because reaction is very slow under normal conditions. However ΔH for this conversion can be calculated from heats of combustions of graphite and diamond measured at the same temperature (25°C) and pressure (1 atm):



Notice if we reverse the second equation and add it in first equation, we get the desired reaction.



Thus the enthalpy of diamond is 1.9 kJ/mole greater than graphite at 25°C and one atm pressure. Therefore, thermodynamic properties of two substances can be properly compared by using a common reference state (standard state).

11.5.1. Conditions for Standard Heat of Reaction

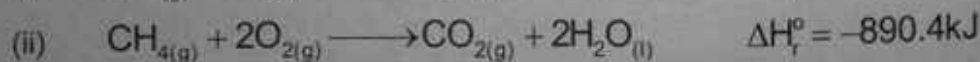
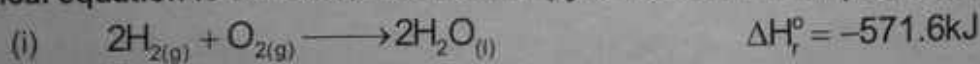
As ΔH varies with conditions, we use standardized ΔH values. These values are calculated when all the substances are in their standard state. Conditions for the standard states are as follows:

1. Standard state for a gas is 1 atm.
2. Standard state for an element or a compound is the most stable physical state at 1 atm and 25°C (298 K).
3. Standard state for a substance in aqueous solution is 1M concentration.

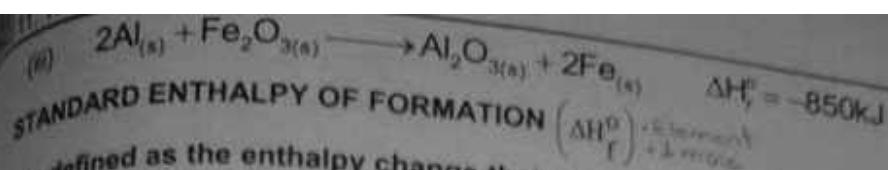
Now we will define important enthalpies.

1. STANDARD ENTHALPY OF REACTION (ΔH_r°)

The enthalpy change in a chemical reaction, when reactants and products are in their standard states and their molar quantities are same as shown by the balanced chemical equation is called standard enthalpy of reaction. Examples are given below:



The student should be guided to remember the information.



STANDARD ENTHALPY OF FORMATION (ΔH_f°)

It is defined as the enthalpy change that accompanies the formation of one mole of a compound from its elements with all substances in their standard states. Standard enthalpies of formation of some compounds are shown in table 11.1.

Table 11.1: Standard enthalpies of formation of some compounds in kJ mole^{-1}

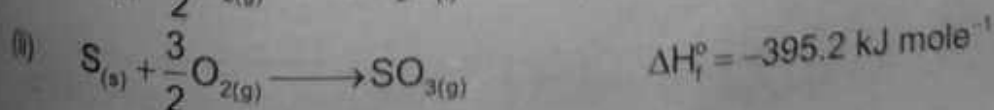
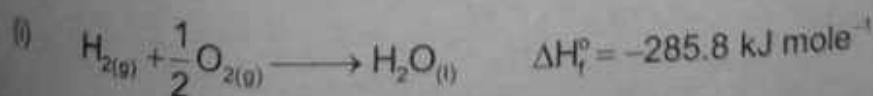
$\text{H}_2\text{O}_{(l)}$	-245.1	$\text{Fe}_2\text{O}_{3(s)}$	-824.2	$\text{Na}^+_{(aq)}$	-240.1
$\text{H}_2\text{O}_{(g)}$	-285.8	$\text{Fe}_2\text{O}_{3(s)}$	-824.2	$\text{Na}^+_{(aq)}$	-240.1
$\text{CO}_{(g)}$	-187.8	$\text{SiO}_{2(s)}$	-910.9	$\text{K}^+_{(aq)}$	-252.4
$\text{CO}_2_{(g)}$	-46.1	$\text{CaCO}_{3(s)}$	-1207	$\text{Mg}^{2+}_{(aq)}$	-466.9
$\text{HNO}_3_{(l)}$	-80.3	$\text{BaCO}_{3(s)}$	-1219	$\text{Ca}^{2+}_{(aq)}$	-542.8
$\text{HNO}_3_{(aq)}$	50.6	$\text{NaOH}_{(s)}$	-425.6	$\text{Al}^{3+}_{(aq)}$	-524.7
$\text{Fe}_{(s)}$	-271.1	$\text{KOH}_{(s)}$	-424.8	C(s, diamond)	1.9
$\text{O}_2_{(g)}$	-92.3	$\text{HONO}_{2(l)}$	174.1	$\text{CH}_4_{(g)}$	-74.8
$\text{H}_2\text{O}_{2(l)}$	167.2	$\text{HONO}_{2(aq)}$	-207.4	$\text{C}_2\text{H}_2_{(g)}$	226.7
$\text{H}_2\text{O}_{(l)}$	-36.4	$(\text{HO})_2\text{SO}_{2(l)}$	-814.0	$\text{C}_2\text{H}_4_{(g)}$	52.3
$\text{H}_2\text{O}_{(g)}$	26.5	$(\text{HO})_2\text{SO}_{2(aq)}$	-909.3	$\text{C}_2\text{H}_6_{(g)}$	-84.7
$\text{NH}_3_{(g)}$	-20.6	$\text{NH}_4\text{Cl}_{(s)}$	-314.4	$\text{C}_3\text{H}_8_{(g)}$	-103.9
$\text{H}_2\text{O}_{(l)}$	-110.5	$\text{NaCl}_{(s)}$	-411.2	$\text{C}_4\text{H}_{10(g)}$	-126.2
$\text{H}_2\text{O}_{(g)}$	-393.5	$\text{NaBr}_{(s)}$	-361.1	$\text{C}_6\text{H}_6_{(l)}$	49.0
$\text{H}_2\text{O}_{(l)}$	90.3	$\text{NaI}_{(s)}$	-287.8	$\text{C}_6\text{H}_5\text{CH}_3_{(l)}$	12.1
$\text{H}_2\text{O}_{(g)}$	33.2	$\text{KCl}_{(s)}$	-436.8	$\text{C}_8\text{H}_{18(l)}$	-249.9
$\text{H}_2\text{O}_{(l)}$	9.2	$\text{KBr}_{(s)}$	-393.8	$\text{CH}_3\text{OH}_{(l)}$	-238.7
$\text{H}_2\text{O}_{(g)}$	-296.8	$\text{KI}_{(s)}$	327.9	$\text{C}_2\text{H}_5\text{OH}_{(l)}$	-277.7
$\text{H}_2\text{O}_{(l)}$	-395.7	$\text{AgCl}_{(s)}$	-127.1	$\text{CH}_3\text{CHO}_{(l)}$	-192.3
$\text{H}_2\text{O}_{(g)}$	-601.7	$\text{CaCl}_2_{(s)}$	-795.8	$\text{CH}_3\text{COCH}_3_{(l)}$	-248.1
$\text{H}_2\text{O}_{(l)}$	-635.1	$\text{AlCl}_3_{(s)}$	-704.2	$\text{CH}_3\text{COOH}_{(l)}$	-484.5

For writing thermochemical equation for enthalpy of formation, write elements as reactants and 1 mole of the compound as product. Show standard states of all the substances. Finally balance the atoms.

Example 11.1

Write thermochemical equation for the formation of H_2O , SO_3 and H_2O_2 . Use data given in table 11.1.

SOLUTION:





Standard enthalpies of formation of some substances are shown in table 11.1.

3. STANDARD ENTHALPY OF COMBUSTION $\left(\Delta H_c^\circ \right)$

$\Delta H_c^\circ = \frac{\Delta H^\circ_{\text{product}} - \Delta H^\circ_{\text{reactant}}}{\text{1 mole of reactant}}$
 + burning in the presence of O_2

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion. Standard enthalpies of combustion of some substances are shown in table 11.2.

Table 11.2 Standard enthalpies of combustion in kJ mole^{-1}

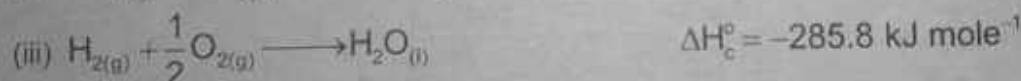
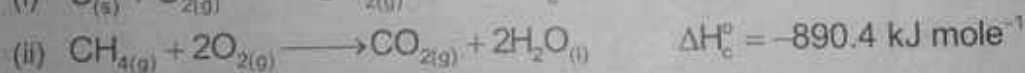
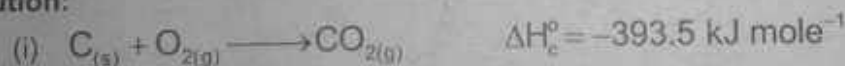
$H_{2(g)}$	-285.8	$CH_{4(g)}$	-890.4	$C_6H_{6(l)}$	-3268
$C(\text{graphite})$	-393.5	$C_2H_6(g)$	-1560	$C_2H_5OH(l)$	-1367
$C(\text{diamond})$	-395.4	$C_8H_{18(l)}$	-5512	$CH_3CHO(l)$	-1167
$S(\text{rhombic})$	-296.9	$C_2H_4(g)$	-1411	$CH_3COOH(l)$	-875
$S(\text{monoclinic})$	-297.2	$C_2H_2(g)$	-1300	$C_6H_{12}O_6(s)$	-2802
			(glucose)		

For writing thermochemical equation for enthalpy of combustion, write 1 mole of the element or compound and oxygen as reactant. Write oxides of the given element or oxides of elements present in the compound as products. Show standard states of all the substances. Finally, balance the atoms.

Example 11.2

Write thermochemical equation for the combustion of, C, CH_4 and H_2 . Use data given in 11.2.

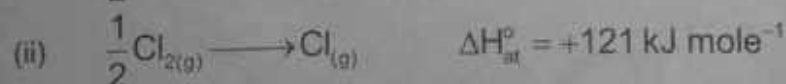
Solution:



4. STANDARD ENTHALPY OF ATOMIZATION $\left(\Delta H_{at}^\circ \right)$

+ to form 1 atom

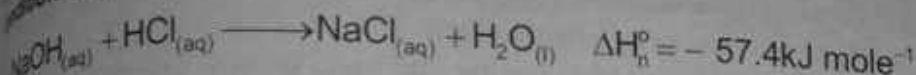
The enthalpy change when one mole of gaseous atoms are formed from its element under standard conditions is called standard enthalpy of atomization. e.g.,



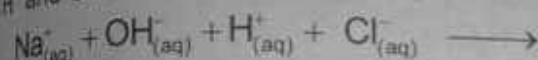
The student should be guided to explain and interpret information.

STANDARD ENTHALPY OF NEUTRALIZATION (ΔH_n°)

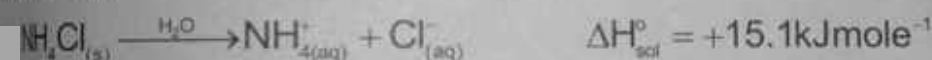
It is defined as the amount of heat evolved when one mole of H^+ ions from an acid combine with one mole of OH^- ions from a base to form one mole of water under standard conditions, e.g.



Strong acids and bases ionize completely in their aqueous solutions. Thus, when solutions of $NaOH$ and HCl are mixed together, the only change which occurs is the formation of water. Na^+ and Cl^- ions remain in solution. Thus heat of neutralization is due to the formation of water from H^+ and OH^- ions.

STANDARD ENTHALPY OF SOLUTION (ΔH_{sol}°)

It is the enthalpy change when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change, under standard conditions, e.g.,



Self Check Exercise 11.2

Write thermochemical equation from the given information: $6C_{(s)} + 3H_{2(g)} \longrightarrow 2C_2H_6(g) \quad \Delta H_f^\circ = +49.0 \text{ kJ}$

Standard enthalpy of formation of benzene (l) is $+49.0 \text{ kJ mole}^{-1}$ $2C_6H_6(l) + 15O_{2(g)} \longrightarrow 12CO_{2(g)} + 6H_2O_{(l)} \quad \Delta H_c^\circ = -277.7 \text{ kJ mole}^{-1}$

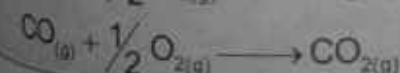
Standard enthalpy of formation of ethanol (l) is $-277.7 \text{ kJ mole}^{-1}$ $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H_c^\circ = -876 \text{ kJ mole}^{-1}$

Standard enthalpy of combustion of acetic acid (l) is $-876 \text{ kJ mole}^{-1}$ $CH_3COOH_{(l)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H_c^\circ = -1367 \text{ kJ mole}^{-1}$

When ethanol is burned in air $-1367 \text{ kJ mole}^{-1}$ energy is released at 1 atm and 25°C . $\Delta H_c^\circ = -1367 \text{ kJ mole}^{-1}$

Which of the following equations describe a reaction for which ΔH° is equal to the

enthalpy of formation of a compound, ΔH_f° $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad \Delta H_c^\circ = -1367 \text{ kJ mole}^{-1}$





11.5.1 Bond Dissociation Energy

When a chemical reaction occurs, old bonds break and new bonds form. Bond breaking always require energy and bond formation always releases energy. **The amount of energy required to break one mole of a particular bond to form neutral atoms is called bond dissociation energy.** Whereas the amount of energy released when one mole of a particular bond form from neutral atoms is called bond energy.

The difference between bond dissociation energy and bond energy determines whether the reaction absorbs or releases energy overall.

For any chemical reaction, the enthalpy change is the sum of bond dissociation energies of the reactants minus the sum of bond energies of products.

$$\Delta H_{\text{reaction}} = \sum \text{B.D.E}_{\text{reactants}} - \sum \text{B.E}_{\text{Products}}$$

For reaction between H_2 and O_2 to produce H_2O :



$$\Delta H^\circ = 2 \times \text{B.D.E of H}_{2(g)} + \text{B.D.E of O}_{2(g)} - 4 \times \text{B.E of O-H bonds}$$

$$= 2 \times (+436 \text{ kJ}) + 493.6 \text{ kJ} - 4 (460 \text{ kJ})$$

$$= 1365.6 \text{ kJ} - 1840 \text{ kJ}$$

$$\Delta H^\circ = -474.4 \text{ kJ.}$$

Thus the reaction between hydrogen and oxygen to form water is exothermic.

11.6 HEAT CAPACITY

When you rub your hands, what happens?

The different forms of energy can be converted into one another. Any other form of energy can be completely transformed into heat energy. But at constant temperature heat cannot be completely converted into another form of energy. Temperature is not the same as heat. Temperature is a property that reflects the random motions of the particles in a substance. Temperature is defined as the measure of average kinetic energy of the molecules of a substance. Heat on the other hand, involves the transfer of energy between two objects due to temperature difference. Temperature difference determines the direction in which heat flows spontaneously. Temperature of a substance does not depend on its mass. But quantity of heat within a substance at a given temperature is directly proportional to its mass. Therefore, amount of heat absorbed by a substance is proportional to the temperature change.

$$q \propto \Delta T$$

$$q = \text{Heat capacity} \times \Delta T$$

Where heat capacity is constant of proportionality, substance.

$$\text{Heat Capacity} = \frac{\text{Heat}}{\Delta T}$$

11. Thermochemistry

297

The amount of heat required to raise the temperature of given amount of a substance by 1 Kelvin is called heat capacity. It is expressed in Joules per Kelvin.

The amount of heat required to raise the temperature of one gram of a substance by 1 Kelvin is called specific heat capacity. It is expressed in Joules per gram per Kelvin.

Water is a major component of living organisms and plants on earth. Its specific heat capacity is very important property for all living beings. Thanks to its high heat capacity, even on very hot days, the heat is generally not high enough to raise the temperature of the internal fluids in animals and plants significantly.

$$\text{Specific heat capacity (c)} = \frac{\text{Heat}}{\text{gram} \times \Delta T} \quad \text{---(2)}$$

The amount of heat required to raise the temperature of one mole of a substance by one Kelvin is called its molar heat capacity. S.I. unit for molar heat capacity is $\text{J.K}^{-1} \text{ mole}^{-1}$.

$$\text{Molar heat Capacity (C)} = \frac{\text{Heat}}{\text{moles} \times \Delta T} \quad \text{---(3)}$$

If the quantity of heat q is absorbed by n moles of the substance and its temperature raises from T_1 to T_2 , its molar heat capacity C is give by the expression.

$$C = \frac{q}{n (T_2 - T_1)}$$

Since heat absorbed by a substance at constant pressure is equal to ΔH .

$$q_p = \Delta H$$

$$\therefore C_p = \frac{q_p}{n(\Delta T)}$$

$$C_p = \frac{\Delta H}{n \Delta T}$$

$$\text{or} \quad \Delta H = n C_p \Delta T$$

Where C_p is molar heat capacity of the substance at constant pressure.

When heat is absorbed by a substance at constant volume, then $q_v = \Delta E$.

$$\text{and} \quad C_v = \frac{q_v}{n \Delta T}$$

$$C_v = \frac{\Delta E}{n \Delta T}$$

$$\Delta E = n C_v \Delta T$$

Where C_v is molar heat capacity of the substance at constant volume.

For Example,

$$\text{Specific heat capacity of Cu} = 0.387 \text{ J.g}^{-1}\text{K}^{-1}$$

$$\text{Molar heat Capacity of Cu} = 0.387 \times 63.54$$

$$= 24.59 \text{ Jmole}^{-1}\text{K}^{-1}$$



Science Titbits

We select materials based on heat capacity to make everyday items such as pots and pans, table ware etc. that are subjected to heat during use. For example it is generally better to use materials with low heat capacity such as metals for cooking utensils, pots or frying pan's to ensure that the heat passes to food faster and to speed up the cooking process.

Knowing specific heat capacity of a substance, its mass and temperature change of substance being heated or cooled, we can determine heat absorb or released.

Re-arranging equation (2) we get,

$$q = C \times m \times \Delta T$$

Similarly, if we know mole of the substance then:

$$q = C \times n \times \Delta T$$

Self Check Exercise 11.3:

- Describe the difference between heat capacity and molar heat capacity.
- Calculate the heat involved when an Al pan weighing 200g is cooled from 100°C to 25°C at constant pressure. Specific heat capacity of Al is $0.9 \text{ Jg}^{-1}\text{K}^{-1}$ (Ans: 13500J)

11.7 CALORIMETRY

Calorimetry is the science of measuring heat of a chemical reaction by measuring the temperature change. **A device that measures heat flow is called calorimeter.** Calorimeters measure the heat released from a system either at constant pressure ($q_p = \Delta H$) or at constant volume ($q_v = \Delta E$). Thus there are two types of calorimetry.

Constant Pressure Calorimetry

In constant pressure calorimetry pressure of the system is fixed. For this purpose we need a thermally insulated container with a thermometer and stirrer. For most purposes a coffee cup calorimeter is used (Fig 11.2).

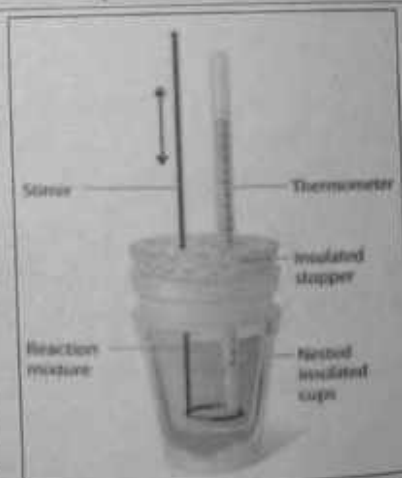


Figure 11.2: Coffee cup calorimeter

$$q = m \times c \times \Delta T$$

Where m = mass of reactants
 C = specific heat of reaction mixture
 ΔT = change in temperature.

11.7.1 ESTIMATION OF HEAT OF REACTION FROM EXPERIMENTAL DATA

This process can be understood by the following example.

11. Thermochemistry

299

In a reaction 50cm^3 of 1.0M NaOH neutralizes 50cm^3 of 1.0M HCl at 25°C . Use this experimental data to calculate the heat of reaction (neutralization) using a calorimeter. Specific heat of water is $4.2\text{Jg}^{-1}\text{K}^{-1}$.

ACTIVITY:

Since neutralization reaction is carried out at constant pressure. We will use coffee cup calorimeter (shown in figure 11.2) to calculate the heat of neutralization in the above example. For this purpose take two nested styrofoam cups. The outer cup will provide extra thermal insulation. Place 50cm^3 of 1.0M NaOH in the inner styrofoam cup and 50cm^3 of 1.0M HCl in a beaker. Keep the two solutions for some time to let them to acquire room temperature. Suppose room temperature is 25°C . Now add slowly the acid solution into the NaOH in the inner cup. The temperature of the solution will rise due to the evolution of heat during the neutralization process. Note down this temperature (suppose it is 31.9°C). Calculate the amount of heat evolved by the following equation.

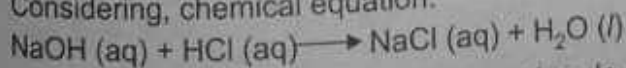
$$\begin{aligned}
 q &= m \times c \times \Delta T \\
 \text{Volume of NaOH} &= 50\text{cm}^3 \\
 \text{Volume of HCl} &= 50\text{cm}^3 \\
 \text{Total Volume of reaction mixture} &= 50\text{cm}^3 + 50\text{cm}^3 = 100\text{cm}^3 \\
 \text{Density of water} &= 1\text{g.cm}^{-3} \\
 \text{Total mass of reaction mixture (m)} &= 100\text{cm}^3 \times 1\text{g.cm}^{-3} = 100\text{g} \\
 \text{Raise in temperature } \Delta T &= 31.9^\circ\text{C} - 25^\circ\text{C} \\
 &= 6.9^\circ\text{C} \\
 &\text{or} \\
 &= 6.9\text{K}
 \end{aligned}$$

$$\begin{aligned}
 q &= m \times c \times \Delta T \\
 q &= 100\text{g} \times 4.2\text{J.g}^{-1}\text{K}^{-1} \times 6.9\text{K} \\
 q &= 2.9 \times 10^3\text{J}
 \end{aligned}$$

$$\begin{aligned}
 \text{No. of moles of NaOH} &= \frac{M \times \text{Vol of solution cm}^3}{1000} \\
 &= \frac{1 \times 50}{1000} = 0.05
 \end{aligned}$$

$$\text{Similarly, No of moles of HCl} = \frac{1 \times 50}{1000} = 0.05$$

Considering, chemical equation.



$$\begin{array}{ccccccc}
 1 \text{ mole} & & 1 \text{ mole} & & & 1 \text{ mole} & \\
 0.05 \text{ mole} & & 0.05 \text{ mole} & & & 0.05 \text{ mole} & \\
 \text{Thus formation of 0.05 moles of water release heat} & & & & & & = 2.9 \times 10^3 \text{ J}
 \end{array}$$

The student should be guided to examine and discuss different parts of the information.

$$\begin{aligned}\text{Formation of 1 mole of water will release heat} &= \frac{2.9 \times 10^3}{0.05} \\ &= 5.8 \times 10^4 \text{ J mole}^{-1} \\ &= 58.0 \text{ kJ mole}^{-1}\end{aligned}$$

Since heat is evolved at constant pressure,

$$q_p = \Delta H_u = -58.0 \text{ kJ mole}^{-1}$$

Self Check Exercise 11.4:

Experimental data shows that when 87.5 cm³ of a 0.10M HCl solution is mixed with 25.0cm³ of 0.35M NaOH in a calorimeter, complete neutralization occurs. The temperature of the calorimeter changes from 25°C to 26.07°C. Use this data to determine heat of neutralization for the reaction.

(Ans: -57.78kJ)

Constant Volume Calorimetry

Constant volume calorimetry is used for accurate determination of the enthalpy of combustion for food, fuel and other compounds. A bomb calorimeter is used for this purpose. Chemical reaction in a bomb calorimeter takes place under constant volume conditions. A bomb calorimeter is shown in fig 11.3. It consists of a strong closed vessel (the bomb) immersed in an insulated water bath.

11.7.2 Estimation of Energy Available from Food

Human beings require three major classes of food (1) carbohydrates (2) fats (3) proteins. Most human energy is derived from carbohydrates and fats. Carbohydrates are the source of quickest energy. Glucose is the simpler carbohydrate, also known as blood sugar. It is soluble in blood and is transported by the blood to all the tissues. In tissues it is oxidized to form CO₂ and H₂O and

energy. We can measure energy available from glucose by determining its heat of combustion. The bomb calorimeter shown in figure 11.3 is used for measuring the energy available from food, which is just the enthalpy of combustion. We can understand this by the following activity.



Figure 11.3: Bomb calorimeter



Activity 1.2

Weigh 1.8 g of glucose and place it in the holder cup of bomb calorimeter and seal it. Adjust the pressure of oxygen in the calorimeter to about 25 atm. Immerse calorimeter in an insulated water bath fitted with a motorized stirrer and a thermometer. Record the temperature of water.



The student must be guided to analyze data.

11. Thermochemistry

301

Suppose it is 25°C. Ignite glucose electrically when it will burn energy will flow from the chemicals to the calorimeter and water. Record the temperature of water again. Thermometer will show 31.52°C. If calorimeter has a total heat capacity of 4.321 kJ K⁻¹. We can calculate energy available from glucose as follows:

$$\text{Increase in temperature} = \Delta T = 31.52^\circ\text{C} - 25^\circ\text{C}$$

$$= 6.52^\circ\text{C}$$

$$\text{Heat evolved} = \Delta T \times \text{total heat capacity of calorimeter}$$

$$= 6.52 \times 4.321 \text{ kJ K}^{-1}$$

$$= 28.1729 \text{ kJ}$$

$$\text{No. Of moles of glucose burnt} = \frac{1.8 \text{ g}}{180 \text{ g.mole}^{-1}}$$

$$= 0.01 \text{ moles}$$

Since 28.1729 kJ of heat was evolved for 0.01 moles of glucose the heat of combustion of glucose per mole

$$= \frac{28.1729 \text{ g}}{0.01 \text{ mole}^{-1}}$$

$$= 2817.29 \text{ kJ mole}^{-1}$$

Thus energy available from glucose is 2817.29 kJ mole⁻¹.

Self Check Exercise 11.5

Fats and oils are a rich source of energy. They provide more energy as compares to carbohydrates and proteins. When 1.0g of a typical fat glycerol trioleate, C₅₇H₁₀₄O₆ is burnt completely in a bomb calorimeter at 25°C raises its temperature by 8.77°C. Total specific heat of calorimeter is 4.321 kJ K⁻¹. List important steps you will use in the determination of heat content of this fat calorimetrically. Calculate also amount of heat available from this fat.

(Ans: 33535.3 kJ mole⁻¹)

11.8 HESS'S LAW

Enthalpy is a state function; therefore, enthalpy change in a chemical reaction in going from some initial state to some final state is independent of the path followed by the reaction. Thus in going from a particular set of reactant to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in many steps. This principle is known as Hess's law.

G.H. Hess stated this law in 1840. It states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.

$$\text{Mathematically} \quad \sum \Delta H (\text{Cycle}) = 0$$

Suppose a reactant A changes into the product B in one step and enthalpy change in this step is ΔH . Now suppose this change takes place in three steps, involving a change from A to C, C to D, and finally D to B as shown below:

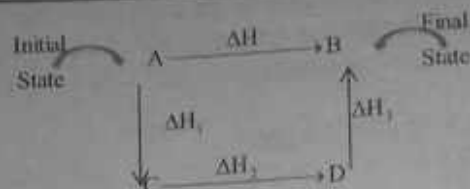


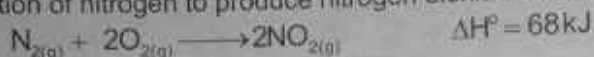
Fig. 11.4

If ΔH_1 , ΔH_2 and ΔH_3 are enthalpy changes in these steps, as shown in the figure (11.4). Then according to the Hess's Law.

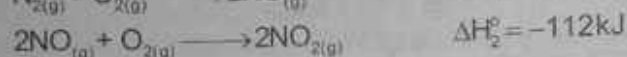
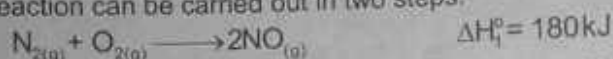
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Example 11.3

Oxidation of nitrogen to produce nitrogen dioxide absorbs 68 kJ of energy.



This reaction can be carried out in two steps.

**Net reaction:**

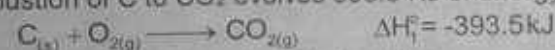
Notice that the sum of two steps gives the net reaction and

$$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 68 \text{ kJ}$$

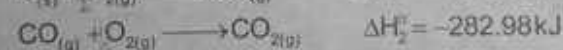
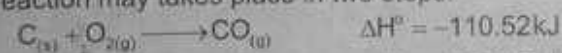
For energy cycle see fig. 11.4.

Example 11.4

Combustion of C to CO_2 evolves 393.5 KJ of energy.



This reaction may takes place in two steps.



Thus the enthalpy change in a chemical reaction is independent of the path followed. Fig. 11.5 shows energy cycle for this reaction.

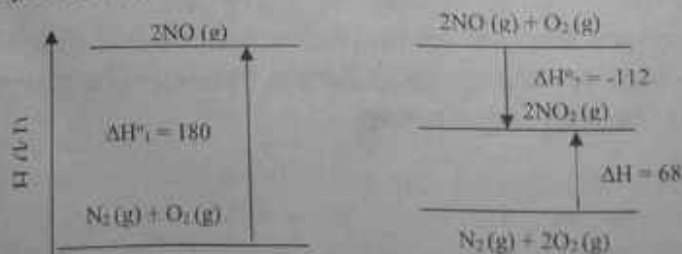


Fig.11.5 (a): Energy cycle for the reaction between $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ to produce $\text{NO}_2(\text{g})$ which steps in this cycle is/are exothermic?

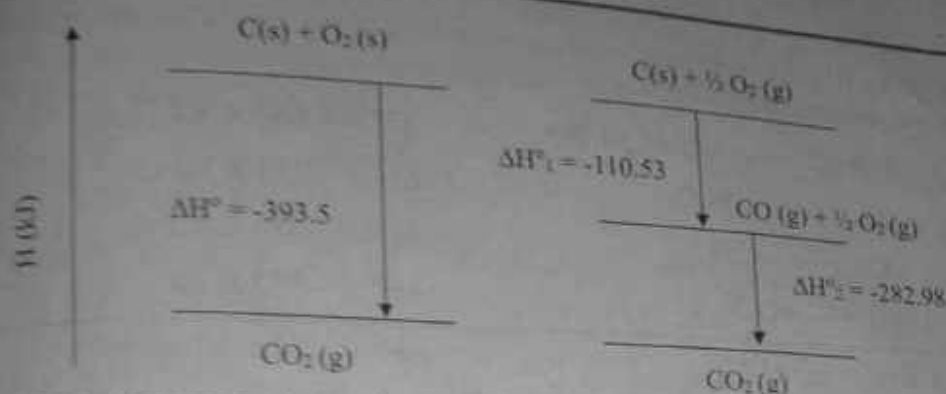
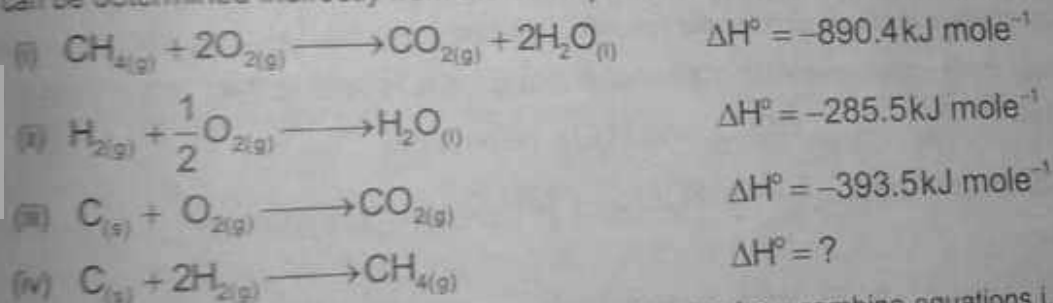


Figure 11.5 (b): Energy cycle for the reaction between $C(s)$ and $O_{2(g)}$ to produce $CO_2(g)$ which steps in this cycle is/are exothermic?

There are many compounds which cannot be prepared directly from their elements. Some of these compounds cannot be decomposed into their constituent elements. e.g. CCl_4 . Some elements do not burn completely due to the formation of a protective covering on their surface. Such as Al, B etc. Thus enthalpies of formation of CCl_4 , Al_2O_3 , B_2O_3 etc cannot be determined directly by calorimetry. Hess's law is particularly useful for determining enthalpies of formation of such compounds.

Example 11.5

Enthalpy of formation of methane cannot be measured directly. By the application of Hess's law it can be determined indirectly from the enthalpies of combustion for CH_4 , H_2 and C.

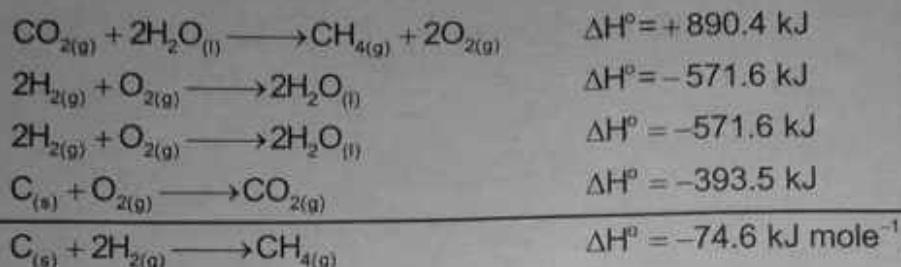


To obtain ΔH° for the required reaction we must somehow combine equations i, ii, and iii to produce that reaction and add the corresponding ΔH° values. This can be done by focusing on reactants and products of the required reaction. The reactants are $C_{(s)}$ and $2H_{2(g)}$ and the product is $CH_{4(g)}$. How can we obtain the correct equation? Reaction (iii) has $C_{(s)}$ as reactant which is needed in the required equation. Thus equation (iii) will be used as such. Equation (i) has $H_{2(g)}$ as reactant but the required equation needs $2H_{2(g)}$, thus equation (ii) will be used after multiplying by 2. Equation (i) has $CH_{4(g)}$ as reactant, but this is needed as product in the



The student must be guided to interpret given information.

required equation. Thus reaction (i) must be reversed and the sign of ΔH° changed according. Adding the equations and deleting the species that occur on both sides we get.



This gives the required equation and its enthalpy.

11.3.1 Enthalpies of Reactions from Enthalpies of Formation

It is often convenient to calculate the ΔH° values for a reaction from values of the standard enthalpies of formation, ΔH_f° of the reactants and products. For a given reaction:

$$\Delta H^\circ = \sum \text{coeff}_p \Delta H_f^\circ (\text{products}) - \sum \text{Coeff}_r \Delta H_f^\circ (\text{reactants})$$

Where coeff = Coefficient

Elements in their standard states are not included in the ΔH° reaction calculation i.e. ΔH_f° for an element in its standard state is zero. When balanced equation for a reaction is multiplied by an integer, the value of ΔH° for that reaction should be multiplied by the same integer.

Example 11.6

Calculate ΔH of reaction for the following reaction, which take place when gasoline burns in internal combustion engines. Where the values of ΔH_f° are -269 kJ, 0 kJ, -393.5 kJ and -285 kJ for $\text{C}_8\text{H}_{18(l)}$, $\text{O}_{2(g)}$, $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(l)}$ respectively



Solution:

$$\begin{aligned}
 \Delta H_{\text{reaction}}^\circ &= \sum \text{coeff}_p \Delta H_f^\circ (\text{products}) - \sum \text{coeff}_r \Delta H_f^\circ (\text{reactants}) \\
 &= [16 \times \Delta H_f^\circ \text{ for } \text{CO}_{2(g)} + 18 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}_{(l)}] - \\
 &\quad [2 \times \Delta H_f^\circ \text{ for } \text{C}_8\text{H}_{18(l)} + 25 \times \Delta H_f^\circ \text{ for } \text{O}_{2(g)}] \\
 &= 16(-393.5 \text{ kJ}) + 18(-285.8 \text{ kJ}) - 2(-269 \text{ kJ}) - 25(0) \\
 &= -6296 \text{ kJ} - 5144.4 \text{ kJ} + 538 \text{ kJ} + 0 \\
 &= -11440.4 \text{ kJ} + 538 \text{ kJ} \\
 &= -10902.4 \text{ kJ} \\
 &= -1.09 \times 10^4 \text{ kJ}
 \end{aligned}$$

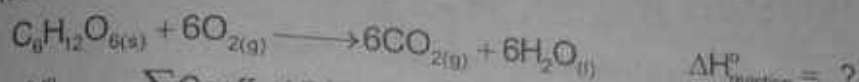


The student must be guided to evaluate the expression.

Example 11.7

Calculate $\Delta H^\circ_{\text{reaction}}$ for the following reaction. This reaction takes place in the tissues of the living organisms. Where the values of ΔH°_f are -1258.18 kJ , 0 kJ , -393.5 kJ and -285 kJ for $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, $\text{O}_2(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ respectively

Solution:



$$\Delta H^\circ_{\text{reaction}} = \sum \text{Coeff}_p \Delta H^\circ_f (\text{products}) - \sum \text{coeff}_r (\Delta H^\circ_f (\text{reactants}))$$

$$\Delta H^\circ_{\text{reaction}} = [6\Delta H^\circ_f \text{CO}_{2(\text{g})} + 6\Delta H^\circ_f (\text{H}_2\text{O}_{(\text{l})})] - [\Delta H^\circ_f \text{C}_6\text{H}_{12}\text{O}_6 + 6\Delta H^\circ_f \text{O}_{2(\text{g})}]$$

$$= [6(-393.5 \text{ kJ}) + 6(-285.8 \text{ kJ})] - [-1258.18 \text{ kJ} + 6 \times 0]$$

$$= [-2361.0 \text{ kJ} - 1714.8 \text{ kJ}] - [-1258.18 \text{ kJ}]$$

$$= -4075.8 \text{ kJ} + 1258.18 \text{ kJ}$$

$$= -2817.62 \text{ kJ}$$

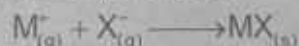
This means one mole (180g) of glucose provides 2817.62 kJ energy. Therefore energy

by one gram of glucose will be $\frac{2817.62 \text{ kJ mole}^{-1}}{180 \text{ g mole}^{-1}} = 15.65 \text{ kJ}$.

11.9 BORN HABER CYCLE

This is special application of Hess's law to binary ionic compounds. It helps us to calculate lattice energies of binary ionic compounds (M^+X^-).

The change in energy that takes place when separated gaseous ions are packed together to form one mole of an ionic solid is called lattice energy.

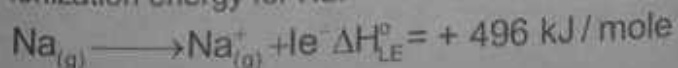


Lattice energy cannot be determined directly. However it can be determined indirectly by means of Born Haber cycle. Consider the case of NaCl. Its standard enthalpy of formation (ΔH°_f) is $-411 \text{ kJ mole}^{-1}$. The formation reaction can be considered as taking place in several steps, one of which is the formation of lattice. This complete sequence of reaction is called a cycle (Fig.11.6)

Step-I: Sublimation of solid sodium. The energy of sublimation for Na(s) is 161 kJ mole^{-1}

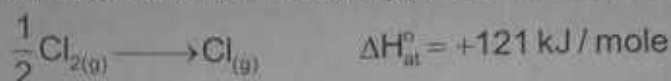


Step-II: Ionization of $\text{Na}_{(\text{g})}$ atom to form $\text{Na}^+_{(\text{g})}$ ion. This process corresponds to the first ionization energy for Na.



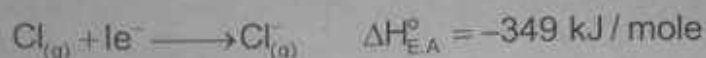
The student must be guided to choose useful information to solve various problems.

Step-III: Dissociation of Cl_2 molecules. We need to form one mole of Cl atoms by breaking the Cl-Cl bond in $\frac{1}{2}$ mole of Cl_2 molecules. The energy required to break this bond is 121 kJ/mole and is known as enthalpy of atomization for Cl_2 .

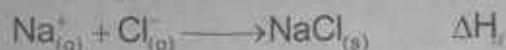


All these three steps are endothermic and are drawn upward in the figure (11.6).

Step-4: Formation of $\text{Cl}_{(g)}^-$ ion. Energy is released in this step equal to the electron affinity for Cl.



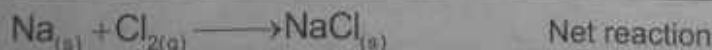
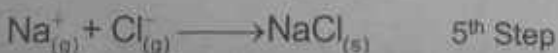
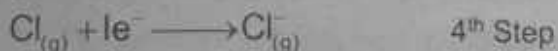
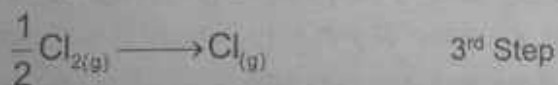
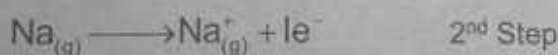
Step-5: Formation of solid NaCl from the gaseous Na^+ and Cl^- ions. This corresponds to the lattice energy (ΔH_f) for NaCl(s) which is to be calculated.



Since the sum of these five steps gives the overall reaction desired, the sum of the individual energy changes give the overall energy change. Thus

$$\begin{aligned} \Delta H_f^\circ &= \Delta H_s^\circ + \Delta H_{\text{I.E}}^\circ + \Delta H_{\text{at}}^\circ + \Delta H_{\text{E.A}}^\circ + \Delta H_f^\circ \\ -411 \text{ kJ} &= +108 \text{ kJ} + 496 \text{ kJ} + 121 \text{ kJ} + (-349 \text{ kJ}) + \Delta H_f^\circ \\ \Delta H_f^\circ &= -411 \text{ kJ} - (108 \text{ kJ} + 496 \text{ kJ} + 121 \text{ kJ} - 349 \text{ kJ}) \\ \Delta H_f^\circ &= -787 \text{ kJ mole}^{-1} \end{aligned}$$

Thus lattice energy of NaCl is 787 kJ/mole.



Electron affinities of atoms are usually calculated from Born-Haber cycle because it is difficult to determine electron affinities directly.

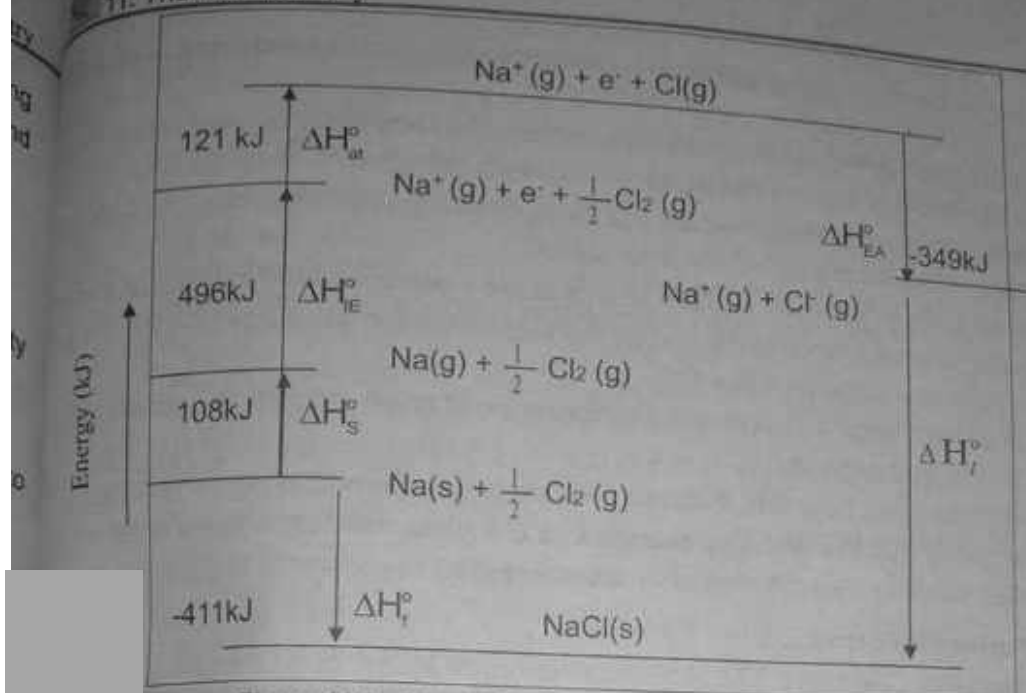


Figure 11.6: Born-Haber Cycle for the formation of NaCl(s)

Self Check Exercise 11.6:

Draw a complete Born Haber Cycle for the formation of MgO(s). Calculate the lattice energy for MgO from the following data.

Standard enthalpy of formation of MgO = $-602 \text{ kJ mole}^{-1}$

Standard enthalpy of sublimation of Mg = 150 kJ mole^{-1}

Ionization energy of Mg(g) to form $\text{Mg}^{2+}(\text{g})$ is $2180 \text{ kJ mole}^{-1}$

Standard enthalpy of atomization of O_2 = 247 kJ mole^{-1}

Electron affinity of O(g) to form $\text{O}^{-1}(\text{g})$ = $-141 \text{ kJ mole}^{-1}$

Electron affinity of $\text{O}^{-1}(\text{g})$ to form $\text{O}^{2-}(\text{g})$ = 878 kJ mole^{-1}

(Ans: -3916 kJ)

Summary of the Key Terms

- The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.
- A chemical reaction that proceeds with the evolution of heat is called an exothermic reaction.
- A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction.
- The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.

The Student be guided to demonstrate skills to distinguish between different parts of calculations and analyse given data.

- The study of all types of energy changes associated with chemical and physical changes is known as thermodynamics.
- The condition of a system when various properties like temperature, pressure, volume, number of moles etc of system have definite values is called state of the system.
- The properties that are determined by the state of the system regardless of how that condition was achieved are called state functions.
- The sum of all kinds of energies of the particles of the system is called as internal energy.
- Thus, enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume ($H = E + PV$).
- The amount of heat required to raise the temperature of given amount of a substance by 1 Kelvin is called heat capacity.
- A device that measures heat flow is called calorimeter.
- Hess's Law states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.

References for Further Information:

- Martin Silberberg, Chemistry, The Molecular Nature of Matter and Change
- Steven S. Zumdahl, Chemistry
- Olmsted Williams, Chemistry, The Molecular Science
- Bonder Pardue, Chemistry, An experimental Science
- Darrell D. Ebbing, R.A.D Wentworth, Introductory Chemistry.
- Raymond Chang, Essential Chemistry
- Graham Hill and John Holman, Chemistry in context



Exercise

1. Choose the Correct Answer

- Which of the following substances have zero value for their standard enthalpy of formation.
 (a) O_3 (b) H_2O (c) ZnO (d) None of these.
- Calorie is equivalent to
 (a) 4.18J (b) 4.18kJ (c) 0.418J (d) 0.418kJ.
- Enthalpy of neutralization of all the strong acids and strong basis has the same value due to
 (a) The formation of salt and water
 (b) The formation of salt
 (c) The complete ionization of acids and bases
 (d) The combination of H^+ and OH^- ions to form water.
- Total heat content of a system is called
 (a) Enthalpy (b) Internal energy (c) Heat (d) State function

11. Thermochemistry

309

- (v) Heat of _____ of a substance is always negative
 (a) Formation (b) Combustion
 (c) Decomposition (d) Solution
- (vi) A balloon filled with oxygen is placed in a freezer. Identify system
 (a) Balloon (b) Oxygen (c) Freezer (d) All of these
- (vii) A bomb calorimeter is used in _____ calorimetry
 (a) Constant volume (b) Constant pressure
 (c) Both a and b (d) Constant temperature
- (viii) Born-Haber cycle is used to determine lattice energies of
 (a) Molecular solids (b) Ionic solids
 (c) Covalent solids (d) Metallic solids
- (ix) $q = \Delta H$ when
 (a) $\Delta V = 0$ (b) $P = 0$ (c) $\Delta E = 0$ (d) None of these
- (x) Enthalpy of combustion for C is $-393.5 \text{ kJ mole}^{-1}$
 $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$ $\Delta H^{\circ}_{\text{Combustion}} = -393.5 \text{ kJ mole}^{-1}$
 Enthalpy of formation of CO_2 would be
 (a) $+393.5 \text{ kJ}$ (b) -393.5 kJ (c) Zero
 (d) Cannot be predicted from the given equation.
- (xi) Which of the following is not a state function of a system.
 (a) Thermal energy at constant pressure
 (b) Enthalpy
 (c) Internal energy
 (d) Work done
- (xii) For writing a thermochemical equation for enthalpy of combustion of an element requires,
 (a) 1 mole of element as reactant
 (b) 1 mole of oxide of element as product
 (c) Standard states of all the substances
 (d) Balanced equation of 1 mole of element
1. a 2. a, b 3. a, c, d 4. a, b, c, d

Name and define units of thermal energy

Define the terms system, surrounding, boundary, state function, heat capacity, internal energy, enthalpy of a substance.

Classify reactions as exothermic or endothermic.

Define bond dissociation energy.

Examine how heat of combustion can be used to estimate the energy available from foods.

Apply Hess's law to construct simple energy cycles.

Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure.

When ethanol burns in oxygen, carbon dioxide and water are formed

(a) Write the equation which describes this reaction.

(b) Using the following data, calculate the enthalpy of combustion for ethanol $\text{C}_2\text{H}_5\text{OH}$.

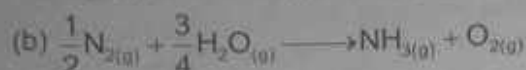
ΔH_f° for ethanol(l) = $-277.0 \text{ kJ mole}^{-1}$

$\Delta H_f^\circ \text{ CO}_{2(g)} = -393.5 \text{ kJ mole}^{-1}$, $\Delta H_f^\circ \text{ water(l)} = -285.8 \text{ kJ mole}^{-1}$

10. Calculate from the data in table 11.1 and 11.2 the enthalpy changes of the following reactions at standard conditions.



(Ans: -49.6 kJ/mole)



(Ans: 382.6 kJ)

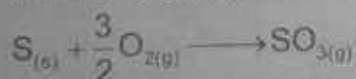
11. The heat of combustion of liquid benzene, C_6H_6 to form H_2O and CO_2 at 1 atm and 25°C is $-3268 \text{ KJ mole}^{-1}$ of benzene. What is the heat of formation of liquid benzene under these conditions.

(Ans: $+49.6 \text{ kJ/mole}$)

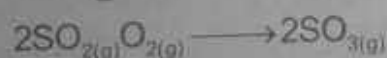
12. Specify conditions for the standard heats of reactions.
 13. Sketch reaction pathway diagram in term of enthalpy changes of the reaction.
 14. State and explain First law of Thermodynamics.
 15. Calculate the work associated with the expansion of a gas from 50dm^3 to 68dm^3 at a constant external pressure of 10 atm.
 16. Camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) has a heat of combustion of 5903.6 KJ/mole . A sample of camphor having mass of 0.1204g is burned in a bomb calorimeter. The temperature increases by 2.28°C . Calculate heat capacity of the calorimeter.
 17. In a coffee-cup calorimeter 100cm^3 of 1.0M HCl and 100 cm^3 of 1.0M NaOH are mixed at 24.6°C raised temperature by 6.9°C . Calculate the enthalpy of neutralization of HCl by NaOH from the given data. Heat capacity of water is $4.18 \text{ J/g}^\circ\text{C}$.
 18. Calculate ΔH° for the reaction



from the following data



$$\Delta H^\circ = -395.2 \text{ kJ}$$



$$\Delta H^\circ = -198.2 \text{ kJ}$$

19. An aluminium frying pan weighs 745g is heated on a stove from 25°C to 205°C . What is q for the frying pan? C_p for Al is $24.35 \text{ J mole}^{-1}\text{K}^{-1}$
 20. Write the balanced equation for the formation reaction of each of the following substances
 (a) $\text{C}_4\text{H}_9\text{OH}$ (Butanol) (b) Rust, Fe_2O_3
 (c) Acetic acid $\text{CH}_3\text{CO}_2\text{H}$ (d) Urea $(\text{NH}_2)_2\text{CO}$
 21. The human body burns glucose for energy. Burning 1.0g of glucose produces 15.65 kJ of heat.
 (a) Write the balanced equation for the combustion of glucose.
 (b) Determine the molar heat of combustion of glucose.
 (c) Heats of combustions of C and H_2 are $-393.5 \text{ kJ mole}^{-1}$ and $-285.8 \text{ kJ mole}^{-1}$ respectively.
 Determine the heat of formation of glucose.

(Ans: 120938.3 J)

(Ans: $-2817 \text{ kJ mole}^{-1}$)

(Ans: -1258.8 kJ/mole)

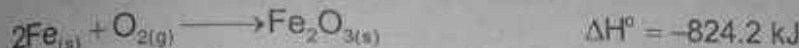
11. Thermochemistry

Sketch the balanced chemical equation associated with each of the following enthalpy changes.

- Heat of sublimation of iodine.
- Heat of formation of gaseous atomic iodine.
- Heat of formation of $C_2H_5Cl_{(g)}$.
- Heat of combustion of benzene $C_6H_{6(l)}$.

24. The standard combustion enthalpies of carbon, hydrogen and acetic acid are $-393.5 \text{ kJ mole}^{-1}$, $-285.8 \text{ kJ mole}^{-1}$ and $-875 \text{ kJ mole}^{-1}$ respectively. Deduce the value of standard enthalpy of formation of acetic acid, CH_3COOH . (Ans: -483.6 kJ/mole)

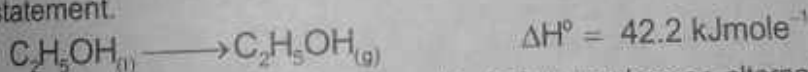
25. Is the conversion of magnetite, Fe_3O_4 to hematite, Fe_2O_3 by oxygen is endothermic or exothermic? Justify your answer.



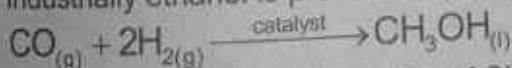
26. Which of the following processes would you expect to be endothermic?

- $H_2O_{(g)} \longrightarrow H_2O_{(l)}$
- $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$
- $Mg_{(g)} + 2e^- \longrightarrow Mg_{(s)}$
- $O_{(g)} + 1e^- \longrightarrow O_{(g)}^{-2}$
- $2Mg_{(s)} + O_{2(g)} \longrightarrow MgO_{(s)}$
- $NaCl_{(s)} \longrightarrow 2Na_{(s)} + Cl_{2(g)}$

27. Cooling effect is experienced when few drops of ethanol are put on your palm, Justify this statement.



28. In some countries liquid methanol is being used as an alternative fuel in cars and trucks. Industrially ethanol is produced by the following reaction.



Standard enthalpies of formation of CH_3OH and CO are $-238.7 \text{ kJmole}^{-1}$ and $-110.5 \text{ kJmole}^{-1}$ respectively. Will the reverse reaction be exothermic or endothermic. Justify (Ans: endothermic)

29. Methane is the major substance in natural gas. How much heat is released when 20 g of methane burns in excess of air under standard conditions. The standard enthalpies formation of CO_2 , H_2O and CH_4 are -393.5 kJ/mole , -285.8 kJ/mole and -74.6 kJ/mole respectively. (Ans: 1113.125 kJ)

30. Evaluate the importance of Hess's Law.



ELECTROCHEMISTRY



After completing this lesson, you will be able to:

- Define cathode, anode, electrode potential and S.H.E. (Standard Hydrogen Electrode).
- Define the standard electrode potential of an electrode.
- Give the characteristics of Redox reaction.
- Define cell potential, and describe how it is determined.
- Determine the oxidation number of an atom of any element in a pure substance.
- Define oxidation and reduction in terms of a change in oxidation number.
- Use the oxidation-number change method to balance redox equation.
- Balance redox reaction into oxidation and reduction half reaction.
- When given an unbalanced redox equation, use the half reaction method to balance the equation.
- Identify the substance oxidized and the substance reduced in a dry cell.
- Describe the reaction that occurs when a lead storage battery is recharged.
- Explain how a fuel cell produces electrical energy.
- Use the activity series of metals to predict the products of single replacement reactions.



Reading

INTRODUCTION

Electrochemistry deals with wide range of important phenomena, many of which depend on the transfer of electrons from one substance to another. **Electrochemistry is the branch of chemistry, which deals with inter-conversion of electrical energy and chemical energy.** Electrochemical processes are redox (oxidation - reduction) reactions in which the energy released by a spontaneous reaction is converted to electricity or in which electrical energy is used to cause a non-spontaneous reaction to occur. Redox reaction involves transfer of electrons from

one substance to another. It deals with efficient sources of energy such as batteries, fuel cells etc. Chemistry of these devices will be discussed in this chapter.

12.1 OXIDATION - REDUCTION CONCEPTS

What happens when an unprotected iron object is left in moist atmosphere for few days? What type of chemical change occurs?

You have learned in your grade IX-X, the definition of oxidation and reduction in terms of loss or gain of oxygen or hydrogen or electrons. Here we will discuss oxidation and reduction in terms of loss or gain of electrons by a chemical reaction in which this change can be observed with naked eyes.

Example 12.2Calculate the oxidation number of Cr in $K_2Cr_2O_7$.**Solution**

$$\begin{array}{rclclcl}
 K_2 & & Cr_2 & & O_7 & & \\
 (+1) 2 + & & (x) 2 + & & (-2) 7 & & \\
 + 2 + & & 2x - & & 14 & = & 0 \\
 + & & 2x - & & 12 & = & 0 \\
 & & & & 2x & = & 12 \\
 & & & & x & = & 12/2 \\
 & & & & x & = & 6
 \end{array}$$

I - A = +1

II - A = +2

III - A = +3

I = -1

O = -2

H = -1 (with metal)

H = +1 (with non-metal)

Thus oxidation number of Cr in $K_2Cr_2O_7$ is +6.**Example 12.3**What is the oxidation state of S in SO_4^{2-} ion.**Solution**In SO_4^{2-} ion oxidation state of O is -2. If x is the oxidation state of S then,

$$x + 4(-2) = -2$$

$$x - 8 = -2$$

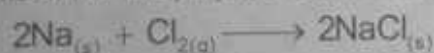
$$x = 6$$

Self Check Exercise 12.1

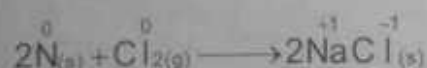
Identify the compound in which oxidation number of Fe is +3

**Oxidation-Reduction in Terms of Change in Oxidation Number**

We have already defined oxidation and reduction in terms of transfer of one or more electrons in section 12.1. We can also define oxidation and reduction in terms of change in oxidation number. For this purpose, consider the following reaction.



Assign oxidation number to all the atoms involved in this reaction and write it over their symbols



Oxidation number of which element is increasing in this reaction? Oxidation numbers of which element is decreasing in this reaction.

Notice that the oxidation number of Na is zero because it is in the elemental form. In this reaction Na undergoes a change in oxidation number from zero in Na to +1 in NaCl. Thus this change can be accounted for by a loss of one electron per Na atom. This is oxidation.



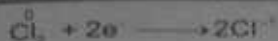
On the other hand, each Cl atom in Cl_2 molecule changes its oxidation number from zero in Cl_2 to -1 in NaCl. In this change gain of one electron per Cl atom occurs. This is reduction.



The Student should be guided to develop skills to interpret information in various ways.

12. Electrochemistry

315



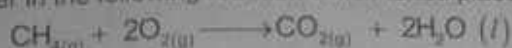
Thus we can also define oxidation and reduction in terms of change in oxidation number.

Oxidation is an increase in oxidation number (a loss of electrons).

Reduction is a decrease in oxidation number (a gain of electrons).

Example 12.4

Identify the elements undergoing oxidation or reduction in terms of change in oxidation number in the following reaction which takes place in the combustion of natural gas.

**Solution**

Assign oxidation number to all the atoms involved in this reaction.



The C changes its oxidation number from -4 in CH_4 to +4 in CO_2 . This is 8 electrons loss.

This means C undergoes an increase in oxidation number. On the other hand, O changes its oxidation number from zero in O_2 to -2 in H_2O and CO_2 . Each oxygen atom gains two electrons and therefore it is reduced.

We can say that,

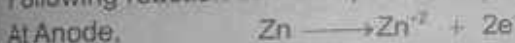
- C is oxidized because there has been an increase in its oxidation number.
- O is reduced because there has been a decrease in its oxidation number.

Example 12.5

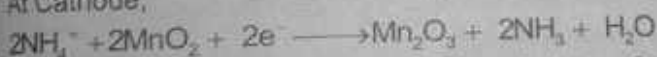
Identify the substance oxidized and the substance reduced in the dry cell.

Solution

Following reaction can take place in dry cell.

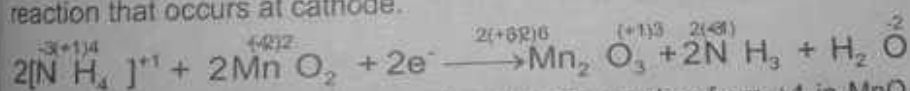


At Cathode,



Anode reaction indicates that Zn metal loses 2 electrons, therefore it undergoes oxidation.

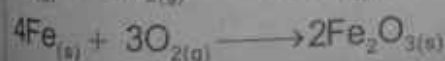
For determining the substance reduced, assign oxidation number to all the atoms involved in the reaction that occurs at cathode.



In this reaction Mn changes its oxidation number from +4 in MnO_2 to +3 in Mn_2O_3 . This means that each Mn gains one electron, therefore undergoes reduction. Thus the substance reduced is Mn.

Self Check Exercise 12.2

Use the oxidation number change method to identify the atoms undergoing oxidation or reduction in the following redox reactions.



12.1.3 Balancing Redox Equations by Oxidation Number Change Method

It is based on the principle that in any redox reaction, the total number of electrons lost by one element must be equal to the total number of electrons gained by another element. This method can be understood by the following example.

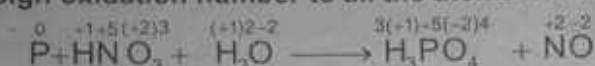
Example 12.6

Balance the following equation by oxidation number method.



Solution

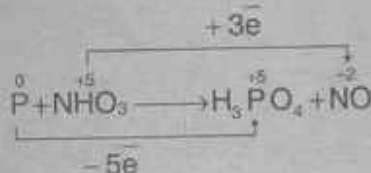
Step1: Assign oxidation number to all the atoms involved in the equation.



Step2: Identify the elements undergoing a change in oxidation number

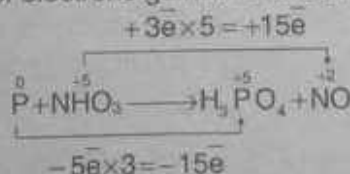
The P goes from zero to +5 oxidation state in H_3PO_4 . This is a 5 electron change. N in HNO_3 goes from +5 to +2 oxidation state in NO. This is 3 electron change.

Step3: Draw a bridge between the same atoms whose oxidation number have changed. Indicate this change by the number of electrons gained or lost by each element.

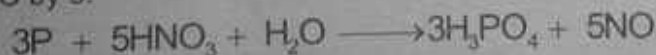


Step4: Equalize the number of electrons lost and gained by multiplying the two numbers, by a small whole number which produces a common number. Use these multipliers as coefficients of the respective substance.

To balance a $3e^-$ gain against a $5e^-$ loss, we need to multiply $3e^-$ gain by 5 and $5e^-$ loss by 3. This will equalize the number of electrons gained and lost.



Multiply the coefficients of P and that of H_3PO_4 by 3. Whereas multiply coefficients of HNO_3 and NO by 5.



Now the coefficient of H_3PO_4 and NO should not be changed hereafter it.

Step5: Balance the rest of the equation by inspection method. Balance the atoms other than oxygen and hydrogen first, then oxygen atoms and finally hydrogen atoms.



The student should be guided to demonstrate this knowledge in various ways.

12. Electrometallurgy
To balance oxygen atoms multiply coefficient of H_2O by 2.
 $3\text{P} + 5\text{HNO}_3 + 2\text{H}_2\text{O} \longrightarrow 3\text{H}_3\text{PO}_4 + 5\text{NO}$
Inspect the equation, it is balanced.

317

Self Check Exercise 12.3

Using the oxidation number method balance the following equation.

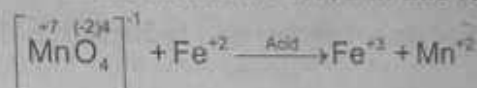


12.1.4 Breaking a Redox Reaction into Oxidation and Reduction Reactions

A redox reaction in aqueous reaction can be separated into two half-reactions. One, half reaction represents oxidation and the other represents reduction. A **half-reaction** is the part of an overall redox reaction that represents, separately, either an oxidation or a reduction. Consider the following reaction which is used to analyze iron ore for its iron content.

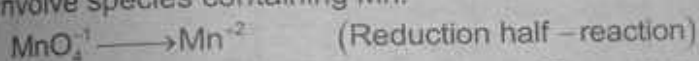


Step 1: Write oxidation number of all the atoms involved in this reaction

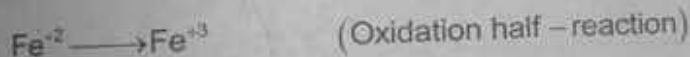


Identify and write equation for the half-reactions.

Notice that the Mn goes from +7 oxidation state in MnO_4^{-1} to +2. The reduction half-reaction must involve species containing Mn.

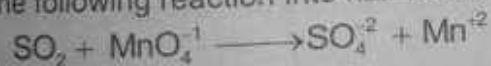


Iron goes from +2 to +3 oxidation state. The oxidation half-reaction must involve Fe^{+2} and Fe^{+3} .

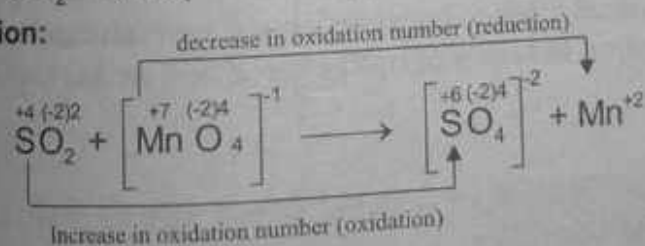


Example 12.7

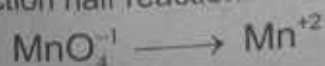
Split the following reaction into half-reactions.



Solution:



Reduction half reaction:



Oxidation half reaction:



The student should be guided to employ this knowledge to illustrate the concepts.

Self Check Exercise 12.4

Split the following reactions into two half reactions:

- (i) $\text{Mn}^{+2} + \text{PbO}_2 \longrightarrow \text{MnO}_4^{-1} + \text{Pb}^{+2}$
 (ii) $\text{Br}_2 + \text{SO}_2 \longrightarrow \text{SO}_4^{-2} + \text{Br}^{-1}$
 (iii) $\text{NO} + \text{MnO}_4^{-1} \longrightarrow \text{NO}_3^{-1} + \text{MnO}_2$

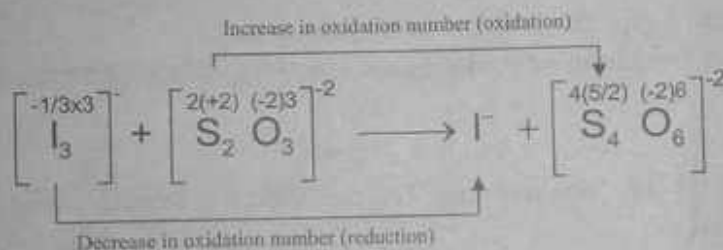
12.1.5 Half Reaction Method to Balance a Redox Reaction

A powerful technique for balancing redox reactions involves dividing these reactions into separate oxidation and reduction half reactions. We then balance the half-reaction, one at a time. And combine them so that electrons are neither created nor destroyed in the reaction.

The steps involved in this method can be understood by considering the following reactions used to determine the amount of the tri-iodide ion (I_3^-) in a solution by titration.



Step1: Break the reaction into oxidation and reduction half-reactions. (as discussed in section 12.1.4)



Reduction half-reaction:



Oxidation half-reaction:



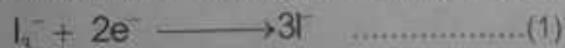
Step2: Balance these half-reactions one at a time. It doesn't matter which half-reaction we balance first. Balance each half reaction in terms of both charge and mass. Let us start with the reduction half reaction.



There are 3 I atoms on the left side and one on the right side. So we will multiply co-efficient of I^- by 3. This will balance I atoms on both the sides.



Now balances charges. The right side has 3 mono negative charges corresponding to -3 charge. But the left side has only one uni negative charge(-1). Thus left side needs $2e^-$.



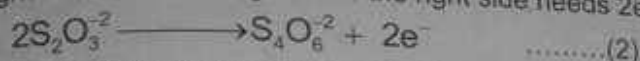
Now balance oxidation half reaction.



To balance S atoms on both the sides, multiply co-efficient of $\text{S}_2\text{O}_3^{2-}$ by 2. This will also balance O atoms.



Now balance charges. The left side has two di negative charges corresponding to $2 \times (-2) = -4$. The right side has -2 charge. Thus the right side needs $2e^-$.



Notice that both the half reaction are balanced in terms of both mass and charge.

Step3: Combine these half reactions so that electrons are neither created nor destroyed. Reduction half reaction uses up $2e^-$ and oxidation half reaction produces $2e^-$, we can therefore obtain a balanced equation by simply adding equation (1) and equation (2)



Step4: Cancel Duplication of Species on both the sides.

Duplications are $2e^-$. Strike these out from both the sides.



Check, the overall reaction is balanced in terms of both charge and mass.

Self Check Exercise 12.5

Use the half reaction method to balance the following redox reactions.

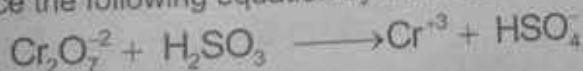


12.1.6 Half Reaction Method to Balance a Redox Reaction in Acid Solution

We can understand this method by the following example.

Example 12.8

Balance the following equation by half reaction method.

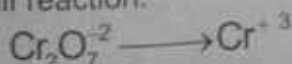


Solution

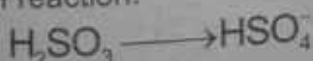
Step1:

Split the reaction into two half reactions.

Reduction half reaction:



Oxidation half reaction:



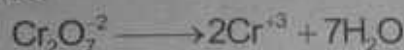
The student should be guided to operate this information in practical uses.

Step2:

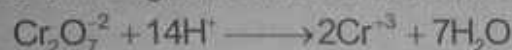
Balance each half reaction. First consider reduction half reaction. Two Cr atoms on the left require 2 before Cr^{+3}



There are seven O atoms on the left and none on the right. So we will add 7 H_2O on the right side.



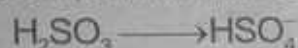
There are 14 H atoms on the right and none on the left, so we will add 14 H^+ on the left side.



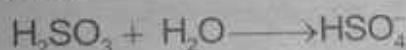
Now balance charges. The left side has one di-negative and 14 mono-positive, corresponding to $-2 + 14 = +12$. The right side has two tri-positive corresponding to $+3 \times 2 = +6$. Thus left side needs $6e^-$.



In the other half reaction (Oxidation half reaction), S atoms are already balanced.



Balance O - atoms. As there are three O - atoms on the left and four on the right, we will add one H_2O to the left.

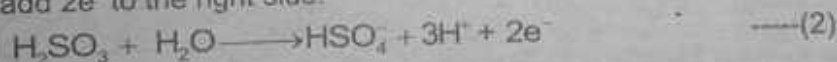


There are four H-atoms on the left and one on the right. We will add 3 H^+ to the right.

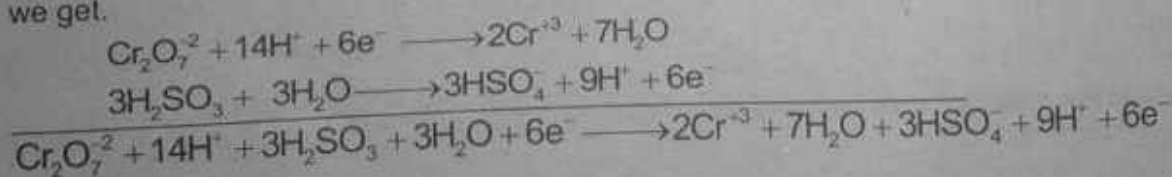


For charge, the left side is neutral but the right side has a net charge of $(-1) + (+3) = +2$.

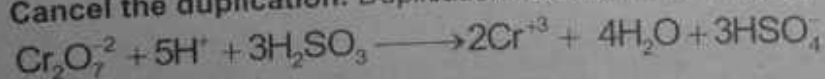
Thus we will add $2e^-$ to the right side.

**Step3:**

Equalize the number of electrons transferred in the two half reactions and add half reactions. Reduction half reaction uses up $6e^-$ and oxidation half reaction produce $2e^-$. Therefore multiplying equation (1) by one and equation (2) by three and adding two equations we get.

**Step4:**

Cancel the duplication. Duplications are $6e^-$, $3\text{H}_2\text{O}$ and 9H^+ . Strike these out from both sides.

**Example 12.9**

Use the half reaction method to balance the following reaction that takes place in acidic medium.



12. Electrochemistry

321

Solution:

Step 1:

Split the reaction into two half-reactions.

Reduction half reaction:



Oxidation half reaction:

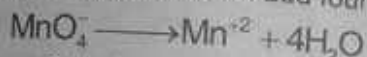


Step 2:

Balance each half reaction. First consider reduction half reaction.



Mn atoms on both the sides are already balanced. There are four O atoms on the left side and none on the right, so we will add four H_2O on the right side.

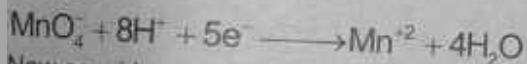


There are 8 H atoms on the right side and none on the left so, we will add 8 H^+ on the left side.



Step 3:

Now balance charges. The left side has one uni-negative and 8 mono-positive charges corresponding to $-1 + 8 = +7$. The right side has one di-positive corresponding to $+2$. Thus left side needs 5e^- .



.....(1)

Now consider oxidation half-reaction.



O atoms on both sides are equal. There are 2H atoms on the left side and none on the right side. So we will add 2H^+ on the right side.



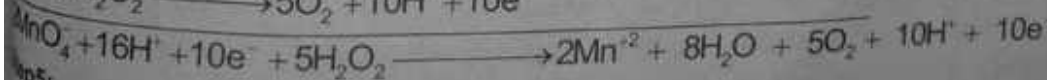
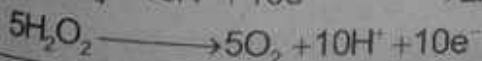
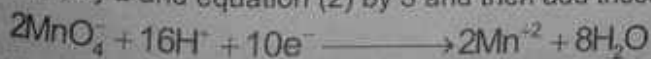
Now balance charges. The left side is neutral whereas the right side has two mono positive charge corresponding to $+1 \times 2 = +2$. Thus the right side needs 2e^- .



.....(2)

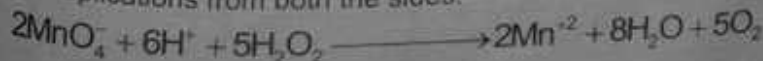
Step 4:

Reduction half reaction uses up 5e^- and oxidation half reaction produces 2e^- . Therefore, multiply equation (1) by 2 and equation (2) by 5 and then add these equations.



Step 5:

Strike out duplications from both the sides.

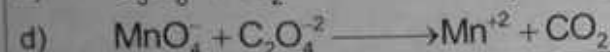
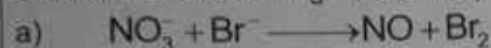


Self Check Exercise 12.6

1. Balance each of the following half reactions that take place in acidic medium.



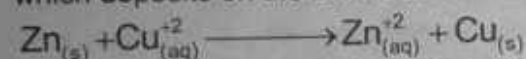
2. Balance the following reactions by half-reaction method, which take place in acidic medium.



12.2 ELECTRODE, ELECTRODE POTENTIAL AND ELECTROCHEMICAL SERIES

12.2.1 The Galvanic Cell

In section 12.1 than have learned that, when a Zn rod is dipped into a copper(II) sulphate solution, zinc atoms are oxidized to zinc ions and copper (II) ions are reduced to copper metal, which deposits on the zinc rod. Following reaction occurs:



In this reaction, electrons flow directly from the zinc rod to Cu^{+2} ions in solution. However, if the electrons transfer from Zinc rod to the copper ions in solution could be directed through an external circuit, the spontaneous redox reaction could be used to generate electric current. But when a zinc rod is dipped in zinc sulphate solution in one container is connected by a copper wire with the copper metal and the copper rod dipped in copper (II) sulphate solution in a separate container, no current flows through the external circuit. However, when the two solutions are connected with a tube (salt bridge) filled with a solution of an electrolyte such as KCl, KNO_3 or Na_2SO_4 , current flows through external circuit.

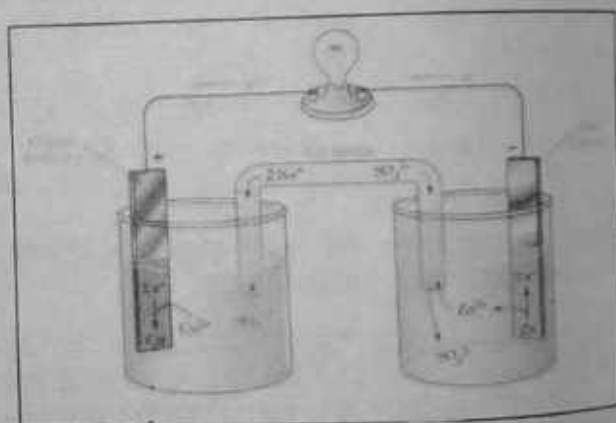


Figure 12.1: A simple Galvanic Cell

The **salt bridge** allows the movement of ions from one solution to the other without mixing of the two solutions and maintains electrical neutrality in each half-cell. (See Fig 12.1)

In one half-cell oxidation takes place and is called as oxidation half-cell or **anode**. Whereas in the other half-cell reduction takes place is called as reduction half-cell or **cathode**. Reaction



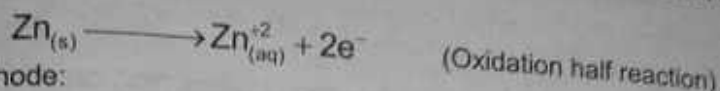
The Students should be guided to express, ability to explain or discuss concepts.

12. Electrochemistry

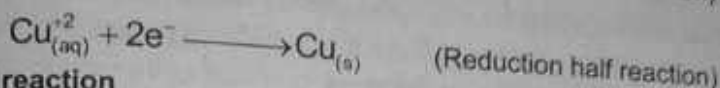
taking place in oxidation half-cell is called oxidation half reaction and the reaction taking place in reduction half-cell is called reduction half reaction.

Zn has greater tendency to lose electrons than Cu. Therefore, Zn electrode acquires negative charge relative to Cu electrode. The electrons flow from Zn electrode through the external circuit to Cu electrode. The following half-cell reactions occur at the two electrodes.

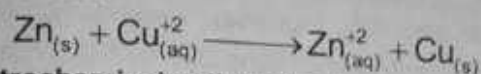
At anode:



At cathode:



Over all cell reaction



An electrochemical cell in which spontaneous redox reaction produces an electric current is known as galvanic or voltaic cell.

The electrode at which oxidation occurs is called the **anode**. Whereas, the electrode at which reduction occurs is called **cathode**.

2 Cell Potential Σ

The cell potential for a galvanic cell is literally the potential of the cell to do work on its surroundings by driving an electric current through a wire. The work that can be accomplished when electrons are transferred through a wire depends upon the push or force behind the electrons.

By definition the force with which electrons are pushed to flow through the wire from anode to cathode is called the electromotive force or emf. It is measured in volts (V). The volt is the measure of energy that is capable of being extracted from the flowing electric charge. When the passage of one coulomb is able to accomplish one Joule of work, then emf is one volt. The emf produced by galvanic cell is called cell potential (E° cell). It depends upon the difference in the electrode potentials of the two half cells joined in series.

Thus the electrode with the more negative reduction potential acts as anode and the electrode with the more positive reduction potential acts as cathode. The net reaction that occurs in the galvanic cell under standard conditions can be constructed from standard reduction half-reactions. Since a redox reaction must include both an oxidation reaction and a reduction reaction, one of the half-cells must run an oxidation that supplies electrons for the reduction. Electrons always flow spontaneously from more negative electrical potential to more positive electrical potential. This means that, under standard conditions, electrons are produced by the reaction with the more negative standard potential and consumed by the reaction with the more positive standard potential. Thus under standard conditions (1 mol dm^{-3} concentration at 25°C and 1 atm pressure), the reaction with more negative E° value occurs as oxidation (anode reaction). The reaction with more positive E° value occurs as reduction (cathode reaction). The

voltage of any cell under standard conditions can be calculated using tabulated standard reduction potentials (see table 12.1).

Any combination of two half-cells will produce a complete cell. The overall cell reaction is obtained by suitably combining the equations for the two half reactions. Standard cell potential E° cell or emf of cell is the algebraic difference between the respective standard reduction potentials of the two half-cells.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

The cell potential has positive value for any spontaneous redox reaction. The potential of a galvanic cell can be measured with a voltmeter. But a single half-cell potential or the **electrode potential** cannot be measured directly. This is because one half-cell reaction cannot occur without a simultaneous reaction in another half-cell. However, relative half-cell potential (electrode potential) can be determined by arbitrarily designating one half-cell reaction and its potential as the standard to which other half-cell potentials are compared. By international agreement, this reference half-cell is the **standard hydrogen electrode**, with the standard potential of 0.00V (for detail see section 12.2.3).

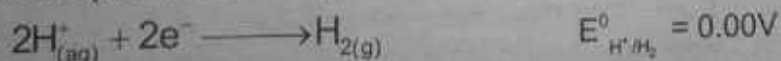
The standard electrode potential is defined as the tendency of a half-cell reaction to undergo reduction relative to the standard hydrogen electrode. It is potential difference developed when an electrode of an element is placed in a solution containing ions of that element when all the components are in their standard state i.e. 1 atm for gases, 1M for solutions, pure solid for electrode and at 25°C.

12.2.3 Standard Hydrogen Electrode

A standard hydrogen electrode (SHE) consists of a platinum foil coated with finely divided platinum, surrounded by hydrogen gas at 1atm pressure in contact with 1M HCl solution at 298K, as shown in Fig 12.2. Its electrode potential is arbitrarily chosen as zero at all temperatures.

By convention, the half-cell potential for reduction of $H^+_{(aq)}$ to H_2 gas or the potential for the oxidation of H_2 to $H^+_{(aq)}$ in the standard Hydrogen half-cell is defined exactly 0.00V.

Reduction: (act as cathode)



Oxidation: (act as anode)

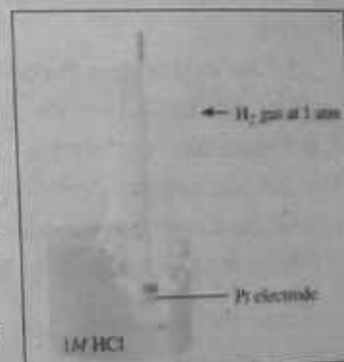
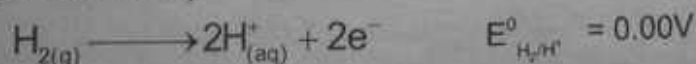


Figure 12.2: Standard Hydrogen Electrode

The student should be guided to examine different aspects of the ideas or concepts.

12. Electrochemistry

The symbol E^0 designates a standard potential i.e., the potential measured under standard conditions (1M concentration, 1 atm pressure and 25°C).

Table 12.1: Reduction potentials of some elements, ions and compounds

Reduction Half-reaction	E^0 (Volts)	
$\text{Li}^+ + \bar{e} \rightleftharpoons \text{Li}$	-3.05	
$\text{K}^+ + \bar{e} \rightleftharpoons \text{K}$	-2.92	
$\text{Ba}^{2+} + 2\bar{e} \rightleftharpoons \text{Ba}$	-2.90	
$\text{Ca}^{2+} + 2\bar{e} \rightleftharpoons \text{Ca}$	-2.76	
$\text{Na}^+ + \bar{e} \rightleftharpoons \text{Na}$	-2.71	
$\text{Mg}^{2+} + 2\bar{e} \rightleftharpoons \text{Mg}$	-2.38	• Oxidation (Anode)
$\text{Al}^{3+} + 3\bar{e} \rightleftharpoons \text{Al}$	-1.67	• produce H_2 with S.H.E
$\text{Mn}^{2+} + 2\bar{e} \rightleftharpoons \text{Mn}$	-1.03	
$2\text{H}_2\text{O} + 2\bar{e} \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.83	
$\text{Zn}^{2+} + 2\bar{e} \rightleftharpoons \text{Zn}$	-0.76	
$\text{Cr}^{3+} + 3\bar{e} \rightleftharpoons \text{Cr}$	-0.74	
$\text{Fe}^{2+} + 2\bar{e} \rightleftharpoons \text{Fe}$	-0.44	
$\text{PbSO}_4 + 2\bar{e} \rightleftharpoons \text{Pb} + \text{SO}_4^{2-}$	-0.36	
$\text{Ni}^{2+} + 2\bar{e} \rightleftharpoons \text{Ni}$	-0.25	
$\text{Sn}^{2+} + 2\bar{e} \rightleftharpoons \text{Sn}$	-0.14	
$\text{Pb}^{2+} + 2\bar{e} \rightleftharpoons \text{Pb}$	-0.13	
$\text{Fe}^{3+} + 3\bar{e} \rightleftharpoons \text{Fe}$	-0.04	
$2\text{H}^+ + 2\bar{e} \rightleftharpoons \text{H}_2$	0.00	
$\text{AgCl} + \bar{e} \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0.22	
$\text{Hg}_2\text{Cl}_2 + 2\bar{e} \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$	+0.27	• Reduction (cathode)
$\text{Cu}^{2+} + 2\bar{e} \rightleftharpoons \text{Cu}$	+0.34	
$\text{Cu}^+ + \bar{e} \rightleftharpoons \text{Cu}$	+0.52	• produce H^+ with S.H.E
$\text{I}_{2(aq)} + 2\bar{e} \rightleftharpoons 2\text{I}^-$	+0.54	
$\text{Fe}^{3+} + \bar{e} \rightleftharpoons \text{Fe}^{2+}$	+0.77	
$\text{Ag}^+ + \bar{e} \rightleftharpoons \text{Ag}$	+0.80	
$\text{Br}_{(aq)} + 2\bar{e} \rightleftharpoons 2\text{Br}^-$	+1.09	

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2ClO_3 + 12H^+ + 5e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$8H^+ + MnO_4^- + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.49
$PbO_2 + SO_4^{2-} + 4H^+ + 4e^- \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.7
$S_2O_3^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.00
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87

12.2.4 Determination of Cell Potential

A cell reaction consists of two half reactions. Reduction takes place in the half-cell having greater value of reduction potential. Oxidation takes place in the half-cell having the smaller value of reduction potential. Equation of the half-cell reaction having smaller value of reduction potential is reversed and added to the equation of half-cell having greater value of reduction potential. Sum of these two equations represent cell reaction.

Example 12.10

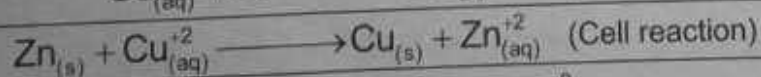
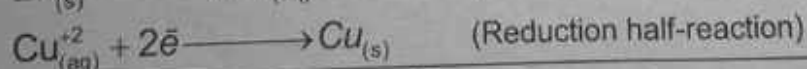
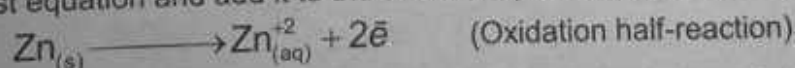
Calculate E^0 cell for Zn-Cu cell and write cell reactions. Show direction of electron flow.

Solution

Half Cell reaction Reduction potential



Data indicates that the reduction potential of second half-cell is greater than the first. Hence reduction reaction will occur in second half-cell and oxidation in the first half-cell. Reverse the first equation and add it to the second equation to get cell reaction.



$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$E_{\text{cell}}^0 = E_{\text{Cu}}^0 - E_{\text{Zn}}^0$$

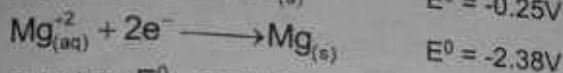
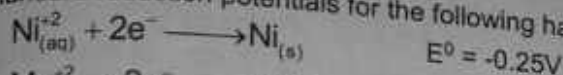
$$E_{\text{cell}}^0 = +0.34 - (-0.76)$$

$$E_{\text{cell}}^0 = +1.10 \text{ V}$$

Electrons will flow from anode to cathode i.e., from Zn electrode to Cu electrode.

Example 12.11

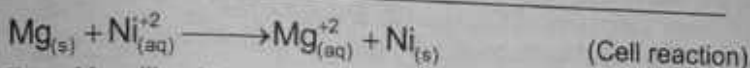
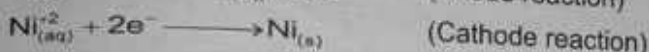
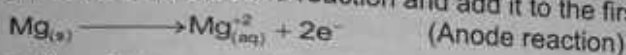
The standard reduction potentials for the following half reactions are:



Calculate E°_{cell} for Ni-Mg cell, write cell reactions, show direction of electron flow and identify the anode of the cell.

Solution:

Data indicates that the reduction potential of first reaction is greater than that of the second reaction. Hence reduction will occur in the first reaction and oxidation in the second reaction. Reverse the second reaction and add it to the first reaction to get the cell reaction.

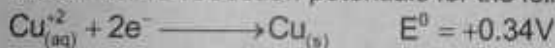


Thus Mg will act as anode and Ni as cathode. Electrons will flow from Mg to Ni.

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Ni}} - E^{\circ}_{\text{Mg}} \\ &= -0.25 - (-2.38) \\ &= 2.13 \text{ V} \end{aligned}$$

Self Check Exercise 12.7

The standard reduction potentials for the following half-reactions are:



Estimate E°_{cell} for Cu-Cl₂ cell, write cell reactions, choose cathode and show the direction of electron flow.

Feasibility of a Chemical Reaction

Whether a chemical reaction feasible or occurs spontaneously, can be inferred from the sign of the sum of E° values of the two half-cell reactions. If this value is positive, reaction occurs spontaneously or will be feasible. The negative value indicates that the reaction is not feasible.

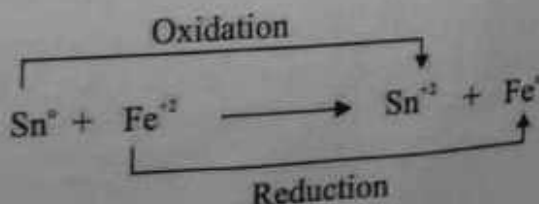
Example 12.12

Is the following reaction feasible?

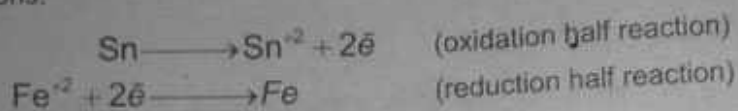


The standard reduction potential values are $E^{\circ}_{\text{Sn}} = -0.14\text{V}$, $E^{\circ}_{\text{Fe}} = -0.44\text{V}$

Solution



It is clear from the above equation that oxidation of Sn and reduction of Fe is taking place. Sn is acting as anode and Fe as cathode. The above reaction consists of the following two half-cell reactions.



$$\begin{aligned}E_{\text{cell}}^0 &= E_{\text{cathode}}^0 - E_{\text{anode}}^0 \\ E_{\text{cell}}^0 &= -0.44\text{V} - (-0.14\text{V}) \\ &= -0.30\end{aligned}$$

As E_{cell}^0 is negative, therefore the given reaction is not feasible. However reverse reaction would be spontaneous.

Self Check Exercise 12.8

Using emf data, argue on the following:

- Can Fe displace Cu from a solution of Copper (II) Sulphate?
- Can Iodine displace Bromine from aqueous solution of Potassium bromide?

Important Information

In modern dentistry, a material most commonly used to fill decaying teeth is known as dental amalgam. Dental amalgam actually consists of Ag, Sn and Hg. the standard electrode potential for this amalgam is +0.67V. Any person who bites a piece of Al foil (such as use for wrapping candies, biscuits etc) in such a way that the foil presses against a dental filling, will experience a momentarily sharp pain. This is because, an electro chemical cell has been created in the mouth, with Al as anode $E^0 = -1.66\text{V}$, the filling as cathode and saliva as electrolyte. Contact between Al foil and filling short circuits the cell. This causes the weak current to flow between the electrodes. This current stimulates the sensitive nerve of the tooth, causing a sharp pain.

12.2.3 Electrochemical Series

Under the recommendation of International Union of Pure and Applied Chemistry (IUPAC) the half-cell reactions are given in the reduction reactions (Table 12.1) therefore E^0 values are known as reduction potentials. However, the value of oxidation potential for an electrode can be obtained by reversing the sign of reduction potential for that electrode. Note that the given reduction potential values relate to standard conditions only, i.e., 1M solution of ions, 25°C (298K) and 1 atm pressure. Changes in conditions will alter these values.

Such a list of arrangement of elements in the order of their standard electrode potential with reference to standard hydrogen electrode is called electrochemical series (Table 12.1).

12.2.4 Activity Series of Metals

A displacement or replacement reaction occurs when an element displaces another element which is a part of a compound. The general equation, $A + XY \longrightarrow X + AY$ in which an atom A replaces atom X in the compound XY illustrate this type of reaction.

For example, if Zn metal is placed in a blue solution of copper (II) sulphate, the blue color slowly fades away and grey metal is replaced by red orange Cu metal. In this reaction Cu ions in the solution are reduced to Cu metal and Zn atoms are oxidized to Zn ions (for details see section 12.1).

12. Electrochemistry

329



However, when copper metal is placed in zinc sulphate solution, no replacement reaction occurs. Table 12.1 shows that the standard reduction potential reaction of copper is greater than that of zinc.

This means that it is easy to oxidize Zn to its ions and reduce Cu^{2+} ions to its atoms. Thus Zn can replace Cu^{2+} ions from its solution. For the same reason Mg and Al can also displace Cu^{2+} ions, but Ag cannot replace Cu^{2+} ions.

Similarly it is observed that metal like Na, K can displace H_2 from water but metals like Cu, Ag cannot displace H_2 from water. Metals are therefore, ranked according to their ability to replace other metals and hydrogen from their compounds. In this ranking metals and hydrogen are arranged in order of decreasing ease of oxidation to their respective ions in aqueous solution.

This arrangement is called **activity series** (see Table 12.2).

Table 12.2 Activity series of common metals

Increases in Reactivity	Li	Very Active metals; React with cold water with the liberation of hydrogen gas; (K and Na react violently with water). They also react violently with acids.
	K	
	Ba	
	Sr	
	Ca	
	Na	
	Mg	Metals of intermediate activity; React with steam or with acids such as HCl with liberation of H_2 .
	Al	
	Mn	
	Zn	
	Cr	
	Fe	
	Cd	
	Co	Moderately active metals React slowly with HCl Do not react with water
	Ni	
	Sn	
	Pb	
	H_2	Moderately noble metal; Do not react with water, HCl but react with oxidizing acids such as HNO_3
	Cu	
	Ag	
	Hg	Very noble metals; React only with aqua regia
	Pt	
	Au	

Important point about the activity series are as follows:

- Metals high on the list transfer electrons to metal cations lower on the list. The greater separation between the species the more vigorous will be the reaction. For example,

The student should be guided to argue his point of view of highlight the conclusion or inference.

when powdered barium is heated with lead (II) oxide, a replacement reaction occurs. This is because Ba is more active than Pb. Barium is oxidized to form barium oxide and lead is reduced to elemental lead.



On the other hand, when iron pellets are added to a solution of MgCl_2 no reaction will occur. This is because Fe is below Mg in the activity series.

2. Very active metals react with cold water to liberate Hydrogen. For example:



3. The less active metals react with steam and with non-oxidizing acid such as HCl. For example:



Al reacts with hot water to a small degree. This is because Al forms a protective coating of Aluminum hydroxide and Aluminum oxide on its exposed surface. This protects metal from further reaction.

4. The moderately active metals such as Co, Ni, Sn, Pb do not react with steam. These metals react spontaneously with 1M HCl.
5. The metals below hydrogen in the activity series do not react with 1 M HCl. These metals are unable to reduce H^+ ions in 1M HCl solution. However, their 1M aqueous ions can be reduced by hydrogen gas at 1 atm. These metals are called as noble metals. The moderately noble metals Cu, Ag and Hg react only with oxidizing acids such as nitric acid and perchloric acids. The very noble metals do not react with these acids but react with aqua regia. For example



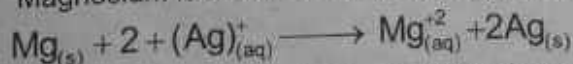
Example 12.13

Predict whether a replacement reaction will occur in the following instances. Defend your conclusion.

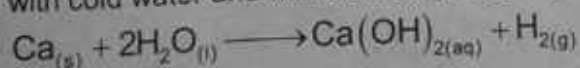
- Magnesium ribbon is in a solution of silver nitrate.
- A small piece of calcium is added to a beaker of water.
- A copper wire is dipped in 1M HCl.

Solution

- Magnesium is above Silver in the activity series. Thus Mg will displace Ag^+ .



- Calcium being very active metal and above hydrogen in the activity list will react with cold water and will liberate hydrogen gas.



- Copper metal is below hydrogen in the activity list, therefore no reaction will take place.

12. Electrochemistry

Self Check Exercise 12.9

Predict whether a reaction occurs in the following cases and write a net ionic equation for the reactions that occurs:

- (i) An iron nail is placed in 1M HCl.
- (ii) Lead(II) oxide is heated with powdered zinc.
- (iii) Nickel wire is placed into a solution of silver nitrate.

331

12.3 TYPES OF ELECTRO-CHEMICAL CELLS

This section is based on your grade IX-X knowledge about electrochemical cells. You have already learnt to sketch these cells.

Devices, which convert electrical energy into chemical energy and vice versa, are known as electrochemical cells. There are two types of electrochemical cells.

- 1) Electrolytic cells.
- 2) Galvanic or voltaic cells.

In these cells electrical energy is used to drive many chemical processes. For example heavy industrial processes such as preparation of sodium hydroxide, metals, purification of nickel and copper, plating of noble metal on jewelry and instruments. The chemical process used in these cells is called electrolysis.

Electrolysis

Electrolysis is the production of a chemical reaction by means of an electric current. The apparatus for an electrolysis consist of an electrolytic cell containing the electrolyte either in molten state or in solution into which two electrodes are placed. The electrodes are connected with a battery. The current is carried from the battery through the wires by mean of electrons (metallic conduction). Within the cell the current is carried by the anions and cations of the electrolyte (Electrolytic conduction). The electrodes serve as a point where conduction changes from metallic to electrolytic or vice versa. At each electrode a chemical reaction takes place in which electrons are gained by the ions in solution at one electrode. Simultaneously electrons are released by some substance at the other electrode. These electrons are returned to the battery through the connecting wire. Thus oxidation-reduction reactions occur at the electrodes. The electrode at which oxidation occurs is called as anode. The electrode at which reduction occurs is called as cathode. The changes, which occur at the electrodes, depend on the relative oxidation-reduction tendencies of the substances involved. You have already learned many examples of electrolysis in grade IX-X. In this section we will discuss quantitative aspects of electrolysis.

The important quantitative aspects of electrochemistry are units, the relation between chemical change and electric current and the relation between tendency for chemical reaction to occur and voltage.

Units

The SI unit of charge is the **coulomb (C)**. It is the charge on 6.25×10^{18} electrons. Although the coulomb is the usual unit for measuring charge, the chemist finds that a more convenient unit is the **Faraday (F)**. It corresponds to the charge carried by the mole of electrons and amounts to 96487 C. The SI Unit of current is the ampere, which is the amount of current flowing when one coulomb passes a given point in one second. Frequently, an ampere is referred as "a coulomb per second".

Relation Between Chemical Change And Electric Current

In 1833, Faraday described the results of his electrochemical investigations by stating the two principles of electrochemistry, which are now known as **Faraday's laws**. The first law of Faraday states that "The amount of chemical reaction taking place at an electrode is directly proportional to the quantity of charge that flows through the electrode during the process."

Second law of Faraday states that, "If same quantity of charge is passed through different electrolytic cells, the chemical change in each case is proportional to the gram equivalent mass of each parent species".

If several cells containing aqueous solutions are connected in series, as shown in figure 12.3 and if 96487 C of charge is passed through them, the electrode reactions proceed simultaneously and for 7.999g of O_2 produced from H_2SO_4 , 1.008g of H_2 , 107.9g of Ag, 31.77g of Cu and 32.5g of Zn are produced at the respective cathodes. These weights are the equivalent

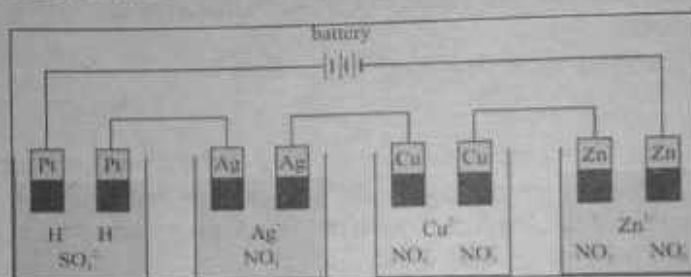


Figure 12.3: Electrolysis of Aqueous Solutions

weights of the respective elements.

It is therefore concluded that 96487 C is the charge on one mole of electrons. This quantity of charge is referred as one Faraday. Thus the quantity of the change that occurs in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500 C. **The amount of a substance produced during electrolysis by passing one Faraday of electricity is called its equivalent weight.**

Example 12.14

In the electrolysis of molten $ZnCl_2$, how much Zn can be deposited at the cathode by passage of 0.01 ampere for one hour?

Solution

$$0.01 \text{ Amp. for one hour} = 0.01 \times 1 \times 60 \times 60 = 36 \text{ C}$$

$$96500 \text{ C/Faraday} = 3.7 \times 10^{-4} \text{ Faraday}$$

In molten Zinc chloride, the cathode reaction is



Which means that for every 2 Faraday of electricity used up, one mole of Zn is deposited. Thus,

$$3.7 \times 10^{-4} \text{ Faraday} \times 1 \text{ Mole of Zn} / 2 \text{ Faradays} = 1.85 \times 10^{-4} \text{ mole of Zn}$$

As one mole of Zn is 63.37g.

$$\text{Therefore } 1.85 \times 10^{-4} \text{ mole of Zn} \times 63.37 \text{ g} = 0.012 \text{ g of Zn. (Ans)}$$



The Student should be guided to distinguish between parts and figures.

12. Electrochemistry

Example 12.15

A constant current was passed through a solution of AuCl_4^- ions between gold electrodes. After a period of 10.0 minutes, the cathode increased in weight by 1.314 grams.

- How much charge was passed?
- What was the amount of current?
- What volume of Cl_2 was collected at anode at 1 atm and 25°C .

Solution

The reaction at cathode is the reduction of Au (III) to Au metal



It means that for every 3 Faraday of electricity used up, 1 mole of Au is produced.

$$\text{Moles of Au} = \frac{1.314\text{gAu}}{197\text{g/mole of Au}} = 6.67 \times 10^{-3}$$

$$\text{Charge} = 6.67 \times 10^{-3} \text{ mole Au} \times \frac{3 \text{ Faraday}}{\text{mole of Au}}$$

$$= 2 \times 10^{-2} \text{ Faraday}$$

$$\text{Current} = \frac{\text{Charge}}{\text{Time(s)}}$$

$$\text{Time} = 10 \text{ mins} = 10 \times 60 = 600\text{s}$$

$$\text{Current} = \frac{(2 \times 10^{-2} \text{F})(96500\text{C/F})}{600\text{s}} = 3.22 \text{ A.}$$

- The reaction at anode is oxidation of Cl^- ions.



For every 2 Faraday of electricity 1 mole of Cl_2 was produced.

For 1 Faraday of electricity = $1/2$ moles of Cl_2 was produced.

For 2×10^{-2} Faraday of electricity = $1/2 \times 2 \times 10^{-2}$ moles of Cl_2 was produced.
 $= 1 \times 10^{-2}$ moles of Cl_2 was produced.

Volume of Cl_2 produced can be calculate by the following formula

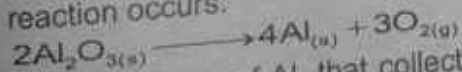
$$V = \frac{nRT}{P}$$

$$= \frac{1 \times 10^{-2} \times 0.08205 \times 298}{1}$$

$$= 0.245\text{dm}^3$$

Self Check Exercise 12.10

- Bauxite ore is used for the commercial preparation of Al . For this purpose bauxite ore is first purified to produced pure alumina, Al_2O_3 . Alumina is then electrolyzed. Following reaction occurs:



Calculate mass of Al , that collects at the cathode and volume of oxygen that collects at node when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C .

- Which of the following compounds will give more mass of metal, when 15 ampere current is passed through molten mass of these salts for 1 hr.
 (a) NaCl (b) CaCl_2

We have already discussed galvanic cells in section 12.2.1. Here we will discuss some important galvanic cells. Batteries are source of direct current and

Redox reactions keep the batteries in our cell phones and laptops functioning.

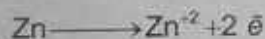
have become essential source of portable power in our society. Batteries provide electric power for starting internal combustion engines in automobiles, for running systems on space vehicles and for such devices as flash lights, toys, heart pacers, electronic calculators, portable radios, TVs, Tape recorders etc. A battery is a galvanic cell or a group of galvanic cell connected in series.

Batteries which can not be recharged are called primary cells e.g. dry cell, whereas batteries which can be recharged are known as secondary cells or storage batteries, e.g. Lead storage battery (automobile battery). A battery can be as tiny as a heart pacemaker implant or as large as the charge storage tanks of an electric automobile. We will discuss some of the important batteries.

1) Dry Cell

The dry cell batteries are used to power many flashlights, toys and small appliances. The anode is the zinc metal of the container and the cathode is an inert graphite rod at the center of the container in contact with a mixture of MnO_2 and carbon (charcoal) see fig 12.4. The electrolyte is a mixture of moist NH_4Cl and ZnCl_2 . Following reactions take place in it,

At Anode

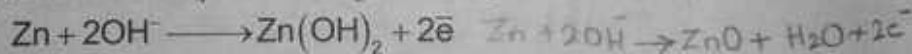


At Cathode



This cell produces a potential of 1.5V. In the alkaline dry cell battery, moist paste of KOH is used as electrolyte instead of NH_4Cl and ZnCl_2 . Following reactions take place in it.

At anode



At Cathode

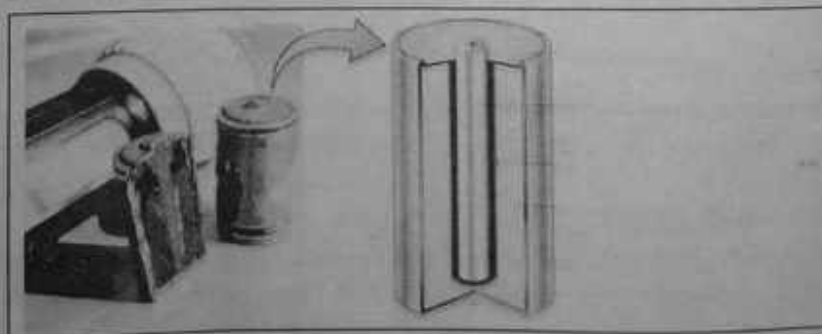
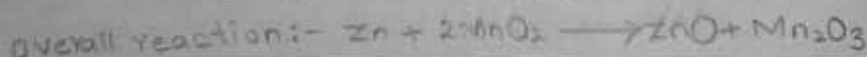
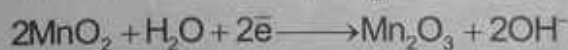


Figure 12.4: A dry cell



The student should be guided appraise significance of the information towards better understanding.

12. Electrochemistry

The alkaline dry cell lasts longer because the zinc anode corrodes less rapidly in basic conditions.

Ni-Cd:

An especially important type of dry cell is the nickel-cadmium battery which has a Cd anode and NiO_2 as cathode. KOH is an electrolyte. Following reactions occur in it.

At anode



At cathode



In this cell, the products adhere to the electrodes. Thus, battery can be recharged.

Lead storage Battery:

The lead storage battery provides electrical power in automobiles. It is well suited for this use because it supplies the large current needed to drive starter motors and headlights and can be recharged easily.

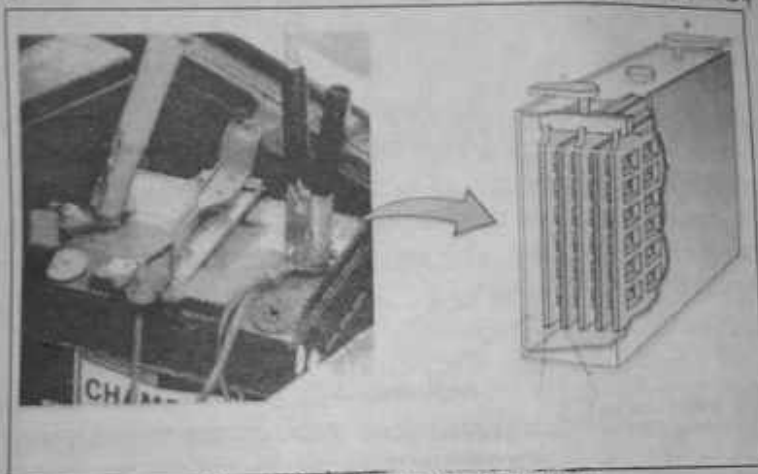
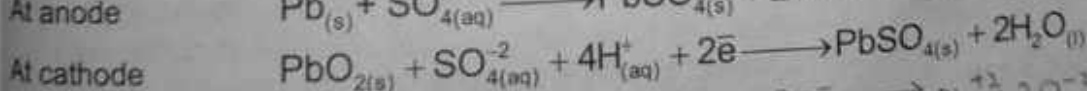
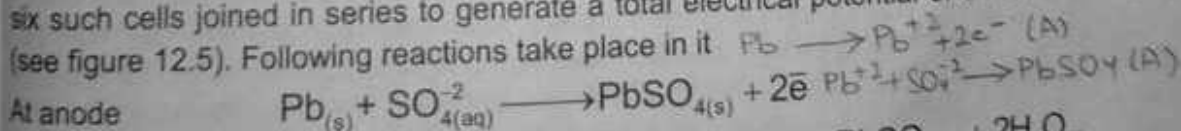
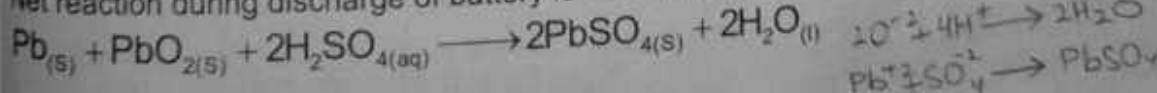


Figure 12.5: A Lead storage battery

The anode is a lead plate that becomes coated with PbSO_4 as the battery discharges. The cathode is lead impregnated with PbO_2 which also becomes coated with PbSO_4 as the battery discharges. Both electrodes are immersed in electrolyte which is 30% H_2SO_4 solution having density 1.25g cm^{-3} . The cell produces potential of two volts. Automobile batteries use three or six such cells joined in series to generate a total electrical potential of 6V or 12V respectively (see figure 12.5). Following reactions take place in it



Net reaction during discharge of battery is



Thus during discharge H_2SO_4 is used up and its density decreases. When both the electrodes are completely covered with PbSO_4 the battery ceases to deliver current until it is recharged.

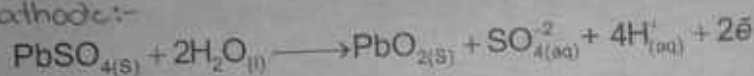
Recharging the Battery

Battery can be recharged by connecting its anode to the negative terminal of direct current and the cathode to the positive terminal of the direct current. Reverse chemical reactions occur at anode and cathode of the battery. Thus deposition of Pb on anode and PbO_2 on cathode take place. The reactions of recharging of battery are as follows.

At cathode Anode :-



At anode Cathode :-



After recharging H_2SO_4 solution is concentrated again bringing density to its initial value of 1.25 g cm^{-3} .

3) Fuel Cell

A fuel cell is a special type of galvanic cell in which reactants are continuously supplied as they are consumed and the products are continuously removed. A fuel cell is based upon the reaction between oxygen and a gaseous fuel hydrogen or methane. We have learnt in section 11.1.3 that when hydrogen burns in air, an exothermic reaction occurs. A lot of chemical energy is released in the form of heat and light. This energy is used for cutting and welding metals. In this reaction hydrogen is oxidized to water.

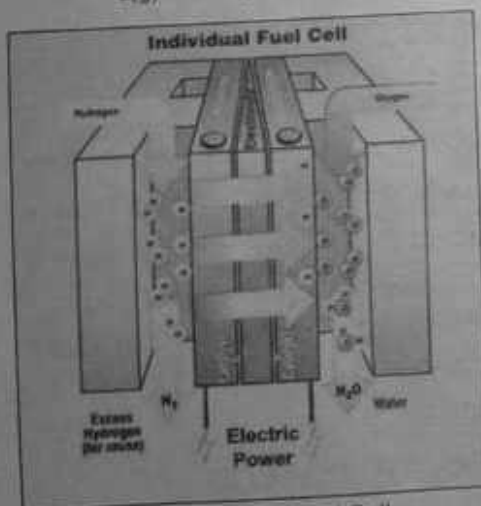
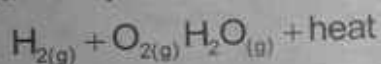
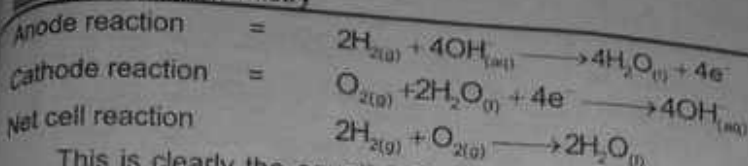


Figure 12.6: A Fuel Cell

However, if this oxidation-reduction reaction is carried in separate compartments connected in series. Electrons released in the oxidation of hydrogen in one compartment begin to flow through the external circuit towards the other compartments. There these electrons bring about reduction of oxygen. Thus electricity begins to flow in the circuit. The energy released from the reaction of hydrogen with oxygen to form water is converted to electrical energy. A hydrogen-oxygen fuel cell has three compartments separated from one another by porous carbon electrodes (see figure 12.6). These electrodes contain platinum as catalyst. The middle compartment contains a hot aqueous solution of KOH. Hydrogen gas is passed through the anode compartment and oxygen is passed through the cathode compartment.

At anode hydrogen is oxidized to water and at cathode oxygen is reduced to hydroxide ions.

12. Electrochemistry



This is clearly the equation for the burning of hydrogen in oxygen but in a fuel cell it is burning without flame. Thus the electrons released in the oxidation of hydrogen flow through the circuit towards the cathode. A hydrogen-oxygen cell delivers 0.9 V. The fuel cell operates at high temperature so the water formed evaporates and may be condensed. The water removed in spacecraft is consumed by the astronauts. The fuel cells of this kind have been used by American space program.

4. Solar Cell

Devices that convert solar energy directly into electric energy are called solar cells. A semiconductor material is used in these cells. This material generates voltage output with light input. A basic solar cell consists of two layer of different types of semi-conductive materials. These materials are joined together to form a junction. When one layer is exposed to light, many electrons acquire enough energy and break away from their parent atoms. Such electrons cross the junction. This means that negative ions are formed on one side of the junction and positive ions are on the other side. Thus a potential difference is developed which causes electrons to flow. Semiconductor made of silicon gives an output of 0.5 V per cell. Research is continuing to get more output with other semi-conductor material. In future solar cells will serve as a cheap source of energy.

13 Corrosion and its Prevention

You have learned definition of corrosion and rusting of iron as an example in your grade. Here we will discuss electrochemical cause of corrosion. We will use e.m.f. data to understand corrosion and its prevention.

Corrosion is a natural process, which converts, refined metals to their more stable metal oxides. The oxidizing agent in corrosion chemistry is atmospheric oxygen. It is most familiar in the form of the rusting of iron. Rusting is an electrochemical process. One of the half reaction in rusting is

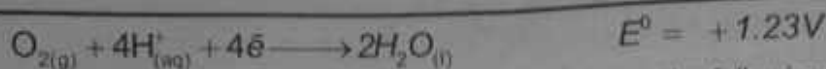


Reverse of this reaction



is driven by the presence of oxygen. Iron (II) is oxidized further to iron (III) and various insoluble hydrated oxides of iron (III) are deposited as the red-brown precipitate known as rust. These oxides are porous, flake off and expose metal to further corrosion. The process of corrosion occurs when metal is in contact with water. The water layer present on the surface of iron or a water droplet on its surface dissolves O_2 and CO_2 . In certain industrial areas where SO_2 or other acidic vapours are present also dissolve. Thus metal comes in contact with the electrolyte. The reduction half reaction is:

The student should be guided to discriminate between the concepts.



is more positive than $\text{Fe}^{+2} - \text{Fe}$ couple, so it can drive the following reaction:



The E^0 cell of the combined half-reactions is

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$E^0_{\text{cell}} = +1.23 - (-0.44)$$

$$E^0_{\text{cell}} = +1.67\text{V}$$

Therefore, there is a strong tendency towards oxidation. Oxidation of iron occurs in an interior region of the droplet whereas reduction of O_2 occurs near the air-droplet interface. (See 12.7)

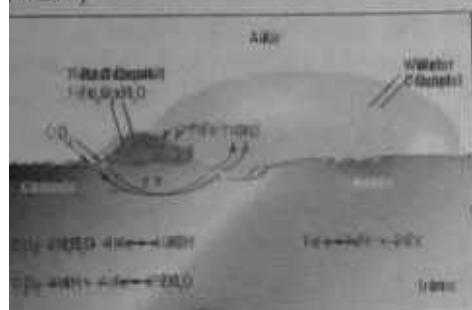


Figure 12.7: Corrosion process of iron

Corrosion cannot be eliminated, but sealing the surface from attacks can slow it down. The corrosion of a metal can be prevented by painting the metal so that it does not come in contact with oxygen and moisture and other harmful agents. Painting also provides visual appeal. That is why bridges, trains, cars etc are painted. A metal surface can also be protected by coating it with a thin layer of a second metal that is less electropositive than the first. This can be done by galvanization or electroplating.

Galvanization

Objects made of iron are dipped in molten zinc and dried. This process is known as **galvanization**. If a scratch penetrates the zinc layer, iron is still protected because Zn oxidizes preferentially. This is because Zn is more active metal than iron, as the potentials for reduction show. Any oxidation that occurs dissolves Zn rather than Fe. Thus Zn acts as sacrificial coating on Fe. This is also known as sacrificial corrosion.

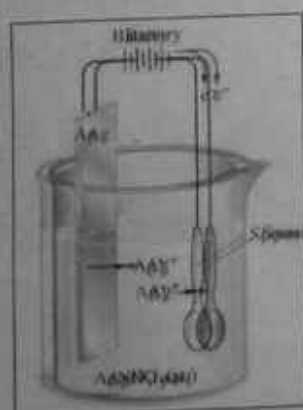


Figure 12.8: Electroplating of silver



Electroplating

Electrolysis can be used to deposit one metal on another. A layer of silver or gold is often plated on jewelry and tableware made from inexpensive metals such as iron. The article to be plated is used as cathode. The metal, which is to be deposited on the article, is used as anode. Water-soluble salt of anode metal is used as electrolyte. When electrical potential is applied, electrons are ejected from anode and move into the cathode (article). Metal ions of anode in solution

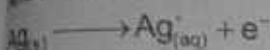
The student should be guided to evaluate the different ideas to discover new facts.

12. Electrochemistry

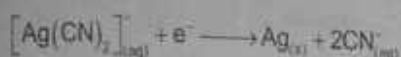
capture the electrons and adhere to the article (cathode). For example, in silver plating, silver is used as anode and sodium cyanide is used as electrolyte. Cyanide ions form a complex with silver ions (see figure 12.8).



Anode reaction



Cathode reaction



Steel objects are often protected from corrosion by electroplating with Aluminum or Chromium. These metals form a thin protective coating of oxide which inhibits further corrosion. The potential of the passive oxide coating is much like a noble metal.

SUMMARY OF KEY TERMS

1. Redox reactions i.e., oxidation and reduction reactions involve the transfer of electrons or change in oxidation numbers.
2. Redox equations can be balanced by using oxidation number method and ion electron method.
3. The driving force behind the spontaneous redox reaction is called the cell potential.
4. The magnitude of cell potential depends upon the conditions under which the measurement is made. Under standard conditions, all solutions have 1M concentration; all gases have partial pressure of 1 atm. The standard potential for the reduction of H^+ to hydrogen gas is arbitrarily taken as zero volts.
5. In a galvanic cell, oxidation and reduction reactions take place at separate electrodes and electron flow through the external circuit. These separate parts of the galvanic cell are half cells. The reactions which occur at these half cells are the half-cell reactions. A salt bridge allows the ions to flow between the half cells.
6. In a galvanic cell, the oxidation occurs at anode and reduction occurs at cathode and the electrons flow in the external circuit from anode to cathode.
7. Voltaic cells use a spontaneous redox reaction to drive an electric current through a wire. Whereas, the electrolytic cells use an electric current to drive a redox reaction.
8. The quantity of electricity carried by 1 mole of electron is called a faraday. It is equal to 96,500 coulombs.
9. In electrolysis electric current from an external source drives a non-spontaneous chemical reaction. The amount of chemical reaction that takes place in electrolysis is directly proportional to quantity of charge transferred at the electrode.
10. A battery is a galvanic cell or a group of galvanic cells connected in series. Some of the well-known batteries are the dry cell, the nickel-cadmium battery, lead-storage battery used in automobiles, fuel cells etc.
11. The corrosion of metals is an electrochemical phenomenon.

References for further learning:

- Bodener and Pardue, chemistry an experimental science 2/e
- Steven s. Zumdahl, chemistry
- Zumdahl, introductory chemistry third edition
- Olmsted and Williams, chemistry, the molecular science
- Silberberg, chemistry, the molecular nature of matter and change

**Exercise****1: Choose the Correct Answer**

- The electrode through which the electron enter the electrolytic solution is
(a) Anode (b) Cathode (c) Salt bridge (d) Electrolyte.
- Oxidation number of S in $\text{Na}_2\text{S}_2\text{O}_3$ is
(a) +1 (b) +2 (c) +3 (d) +4
- In the electrolysis of molten ZnCl_2 , the cathode reaction is $\text{Zn}^{+2} + 2\text{e}^- \rightarrow \text{Zn}$ what quantity of electricity is used up for the production of half mole of Zn
(a) 2 Coulombs (b) 1F (c) 2F (d) 2 ampere
4. How many moles of Cr will be produced by 1.5 Faradays of electricity by the following reaction $\text{Cr}^{+3} + 3\text{e}^- \longrightarrow \text{Cr}$
(a) 0.1 (b) 0.2 (c) 0.03 (d) 1.5 (e) 0.5
- $E^\circ_{\text{Sn}} = -0.14\text{V}$, $E^\circ_{\text{Pb}} = -0.13\text{V}$
(a) Sn^{+2} can oxidize Pb (b) Pb^{+2} can oxidize Sn
(c) Both can oxidize each other (d) Both can reduce each other.
- A fuel cell operates at _____ temperature
(a) Low (b) Medium (c) Room (d) High
- The oxidation number of Cl in HClO_4 is
(a) -1 (b) +1 (c) +5 (d) +7
- In which of the following compounds oxidation number of N is +5
(a) NO_2 (b) N_2O_4 (c) N_2O_3 (d) N_2O_5
- The Passage of current through an electrolyte is due to the movement of
(a) Electrons (b) Anions (c) Cations (d) Ions
- Oxidation number of an element in Free State is
(a) Negative (b) Positive (c) Zero (d) ± 1
- Which of these is not true of an electrolyte.
(a) It can conduct electricity in molten state
(b) It can conduct electricity in the form of aqueous solution.
(c) It can conduct electricity in the solid form.
(d) It can be an acid, a base or a salt.

12. Electrochemistry

- xii. Corrosion is an electrochemical process which requires
- Oxygen
 - Water
 - Acidic vapours
 - Basic vapours

- a
- a, b
- a, b, c
- a, b, c, d

- xiii. A fuel cell is based upon the reaction between

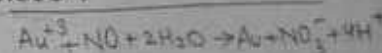
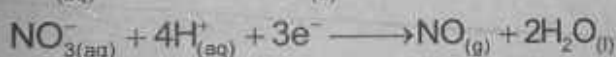
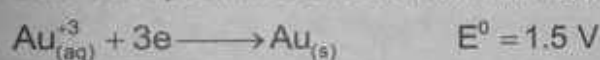
- Oxygen
- Gaseous fuel
- KOH
- Pt

- a
- a, b
- a, b, c
- a, b, c, d

Explain, why?

- Reduction of 1 mole of each Zn^{+2} and Ag^+ require different Faradays of electricity. *due to ion difference*
- It is not possible to measure the potential of an isolated half-cell. *to complete the circuit.*
- The life of a dry cell is shorter than that of an alkaline dry cell.

Write the spontaneous reaction for the following sets of half-reactions.



Explain the following with reasons.

- The oxidation potential of Zn is +0.76V and its reduction potential is -0.76V.
- A salt bridge maintains the electrical neutrality in the cell.
- Na and K can displace hydrogen from acids but Cu and Pt cannot.
- Lead storage battery is rechargeable battery. *reverse the process.*
- Zn plating saves Fe from corrosion.

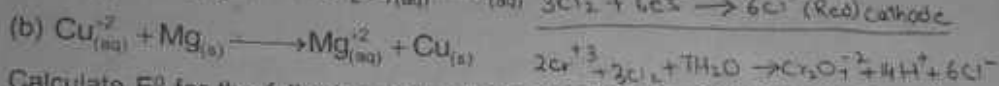
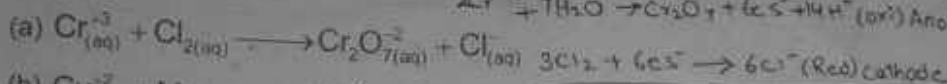
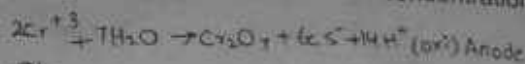
What kind of reaction occurs at the negative terminal of the galvanic cell? *Anode (oxidation)*
Corrosion is often accelerated where the coating on the body of a car has begun to crack, interpret it.

How many hours would electroplating have to be continued at the rate of 5 amperes if 75g of copper is to be deposited from CuSO_4 Solution? $\text{Moles} = \frac{\text{Mass}}{\text{M.Mass}} = 1.18 \text{ moles}$

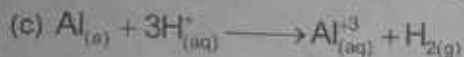
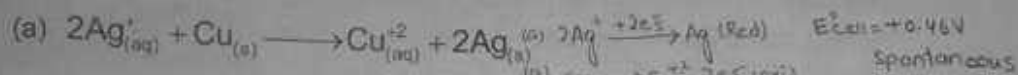
Differentiate between the following

- A galvanic and electrolytic cell
- Oxidation half-reaction and reduction half-reaction

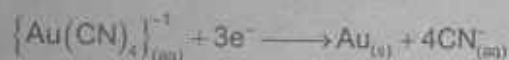
9. Sketch the galvanic cell based on the following overall reaction. Show direction of electron flow and identify the anode, write balanced reaction. Assume all concentrations are 1.0 M



10. Calculate E° for the following cells, which reactions are spontaneous as written under standard conditions.



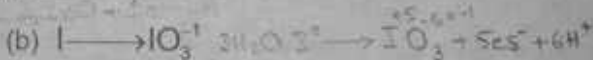
11. An electroplating apparatus is used to coat jewelry with gold. What mass of gold can be deposited from a solution that contains $\{\text{Au}(\text{CN})_4\}^{-1}$ ion if a current of 5.0 amperes flows for 30 minutes, following half-reaction occurs.



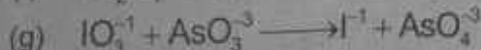
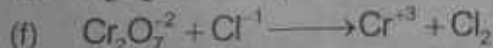
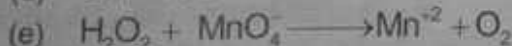
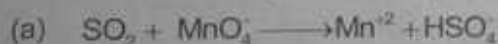
12. Determine oxidation number of all the atoms in the following



13. Balance the following half-reactions

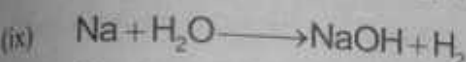
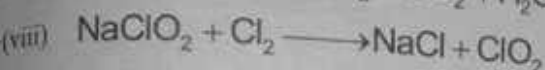
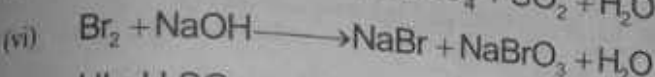
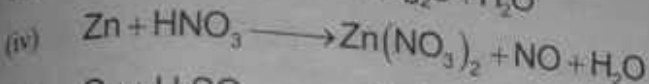
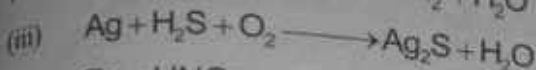
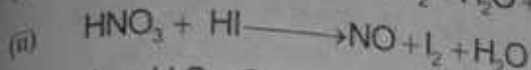


14. Balance the following reactions by ion electron method



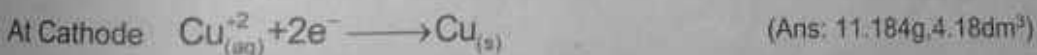
12. Electrochemistry

Balance the following equations by oxidation number method



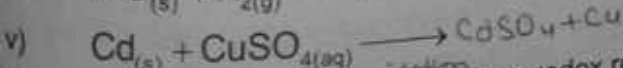
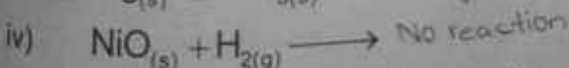
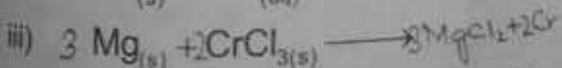
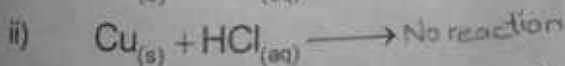
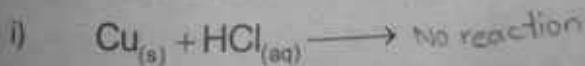
A dead lead storage battery has 5g of PbSO_4 deposited on each of its anodes. It is connected to a charger that supplies 0.12 ampere of current at a voltage of 13V. To which electrode, Pb or PbO_2 should the anode of charger be connected? Write the half reaction occurring at this electrode during charging?

Calculate the mass of Cu and O_2 produced by the electrolysis of CuSO_4 solution on passing 5.0 amperes of current for 2 hrs. What would be the volume of O_2 at S.T.P. Following reactions occurs at the electrodes.

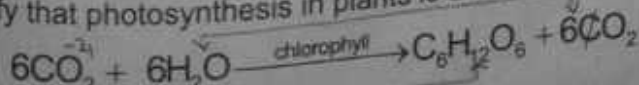


If a chromium steel bicycle handlebar is scratched, exposing steel, will chromium or steel corrode? Chromium will corrode first.

Use the activity series of metals to predict the products of following single replacement reactions. Give reason.



Justify that photosynthesis in plants is a redox reaction.



21. Metal A can displace metal B from its aqueous solution, metal B can displace metal D from its aqueous solution, but it cannot displace metal C from its aqueous solution. Metal C can displace metal A from its aqueous solution. Metals B and D can be displaced from their aqueous solution by hydrogen. Arrange these metals and hydrogen in order of decreasing activity.
22. Differences in the standard potentials of electrodes A and B, B and C are 1.5V and 3.0V respectively.
 $A-B = 1.5V$
 $B-C = 3.0V$
 a) Calculate the cell potential of the working cell between A and C.
 b) Identify cathode in this cell.
23. Standard electrode potentials of three electrodes are in the following order,
 $E_A^0 > E_B^0 < E_C^0$
 Choose anode in the working cell, when (a) Electrodes A and C are joined in series. (b) Electrodes B and C are joined in series (c) Electrodes A and B are joined in series.
24. Evaluate the importance of standard reduction potentials.

22. $A-B = 1.5V$

$A = 1.5 + B$

$B-C = 3.0V$

$C = B - 3.0$

$A-C$

$1.5 + B - B + 3 \Rightarrow 4.5V$

OR,

$E_{cell}^0 A-B = 1.5V$

$E_{cell}^0 B-C =$

$E_{cell}^0 A-C$