ME English Center

New Chemistry Book

Class 11th Notes

(According to new book)

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Chapter 1: STOICHIOMETRY

Multiple Choice Questions

1. Choose the correct answer:

(i) If the volume occupied by oxygen gas (O_2) at STP is 44.8dm³, the number of molecules of O_2 in the vessels are:

(a) 3.01×10^{23} (b) 6.02×10^{23} (c) 12.04×10^{23} (d) 24.08×10^{23}

(ii) The number of carbon atoms in 1 mole of sugar ($C_{12}H_{22}O_{11}$) are approximately:

(a) 6×10^{23} (b) 24×10^{23} (c) 60×10^{23} (d) 72×10^{23}

(iii) In the reaction $2Na + 2H_2O \rightarrow 2NaOH + H_2$, if 23g of Na reacts with excess of water, the volume of hydrogen gas (H_2) liberated at STP should be:

(a) 11.2 dm³ (b) 22.4 dm^3 (c) 33.6 dm³ (d) 44.8 dm^3

(iv) Which of the following sample of substances contains the same number of atoms as that of 20g calcium:

(a) 16g S (b) 20g C (c) 19g K (d) 24g Mg

(v) Which of the following statement is incorrect?

(a) The mass of 1 mole Cl_2 gas is 35.5g

(b) One mole of H_2 gas contains 6.02×10^{23} molecules of H_2

(c) Number of atoms in 23g Na and 24g Mg are equal

(d) One moles of O_2 at S.T.P occupy 22.4 dm³ volume

(vi) For Avogadro's number, this statement is incorrect:

(a) It is the no. of particles in one moles of any substances

(b) Its numerical value is 6.02×10^{23}

(c) Its value change if temperature increases

(d) Its value change if number of moles increases

(vii) The minimum number of moles are present in:

(a) 1 dm^3 of methane gas at STP

(b) 5 dm^3 of helium gas at STP

(c) 10 dm^3 of hydrogen gas at STP

(d) 22.4 dm^3 of chlorine gas at STP

(viii) Number of atoms in 60g carbon are:

(a) 3.01×10^{23} (b) 3.01×10^{24} (c) 6.02×10^{23} (d) 6.02×10^{24}

(ix) Maximum number of molecules present in the following sample of gas:

(a) 100g O_2 (b) 100g CH_4 (c) 100g CO_2 (d) 100g Cl_2

(x) Generally actual yield is:

(a) Greater than theoretical yield

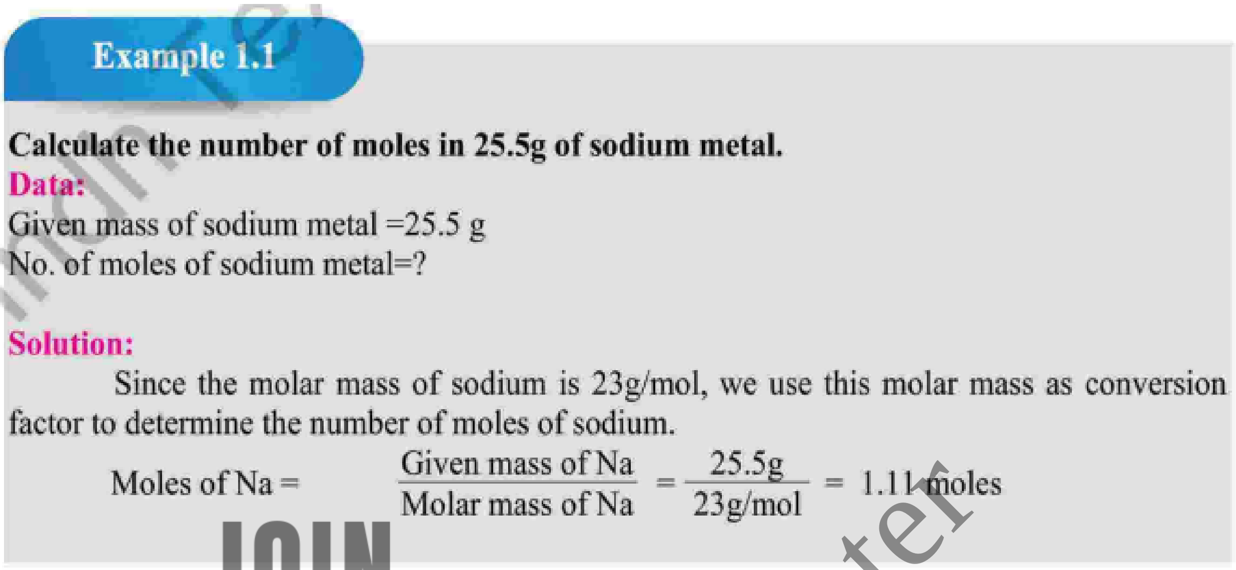
(b) Less than theoretical yield

(c) Equal to the theoretical yield

(d) Some times greater and some times less than theoretical yield

KEY:

i. c	ii. d	iii. a	iv. a	v. a
vi. c	vii. a	viii. b	ix. b	x. b



Example 1.1

Calculate the number of moles in 25.5g of sodium metal.

Data:

Given mass of sodium metal =25.5 g

No. of moles of sodium metal=?

Solution:

Since the molar mass of sodium is 23g/mol, we use this molar mass as conversion factor to determine the number of moles of sodium.

$$\text{Moles of Na} = \frac{\text{Given mass of Na}}{\text{Molar mass of Na}} = \frac{25.5\text{g}}{23\text{g/mol}} = 1.11 \text{ moles}$$

Example 1.2

Calculate the mass of 3.25 moles of water (H_2O).

Data:

Given No. of moles of water = 3.25

Mass of water (H_2O) = ?

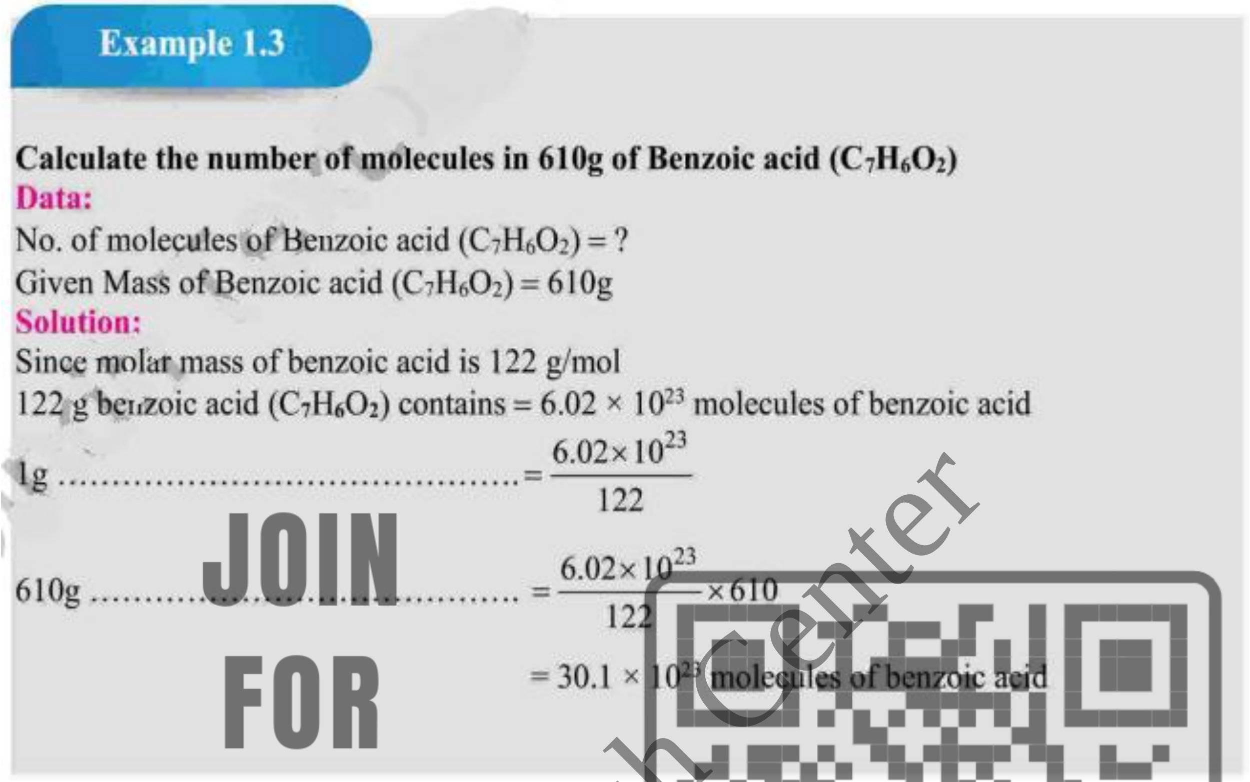
Solution:

To convert mass of water into moles, we use the following relation

$$\text{Moles of water} = \frac{\text{mass of water}}{\text{molar mass of water}}$$

Mass of water = moles of water × molar mass of water

Mass of H_2O = 3.25 × 18 = 58.5g



Example 1.3

Calculate the number of molecules in 610g of Benzoic acid ($C_7H_6O_2$)

Data:

No. of molecules of Benzoic acid ($C_7H_6O_2$) = ?

Given Mass of Benzoic acid ($C_7H_6O_2$) = 610g

Solution:

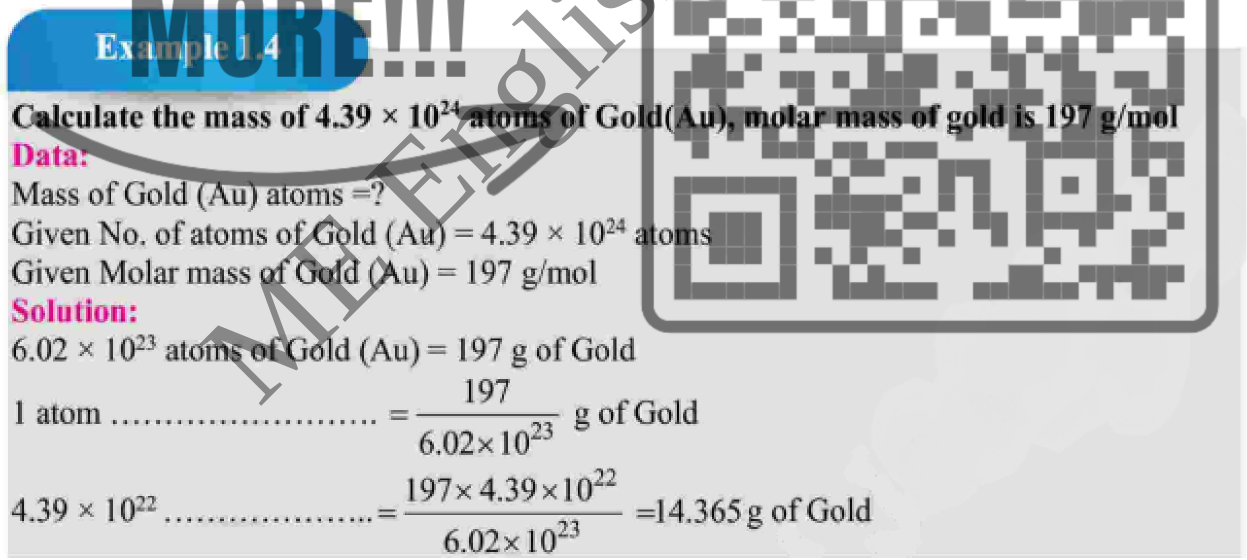
Since molar mass of benzoic acid is 122 g/mol

122 g benzoic acid ($C_7H_6O_2$) contains = 6.02×10^{23} molecules of benzoic acid

1g ………………………………………… $= \frac{6.02\times10^{23}}{122}$

610g ………………………………………… $= \frac{6.02\times10^{23}}{122}\times610$

$= 30.1 \times 10^{23}$ molecules of benzoic acid



Example 1.4

Calculate the mass of 4.39×10^{24} atoms of Gold(Au), molar mass of gold is 197 g/mol

Data:

Mass of Gold (Au) atoms =?

Given No. of atoms of Gold (Au) = 4.39×10^{24} atoms

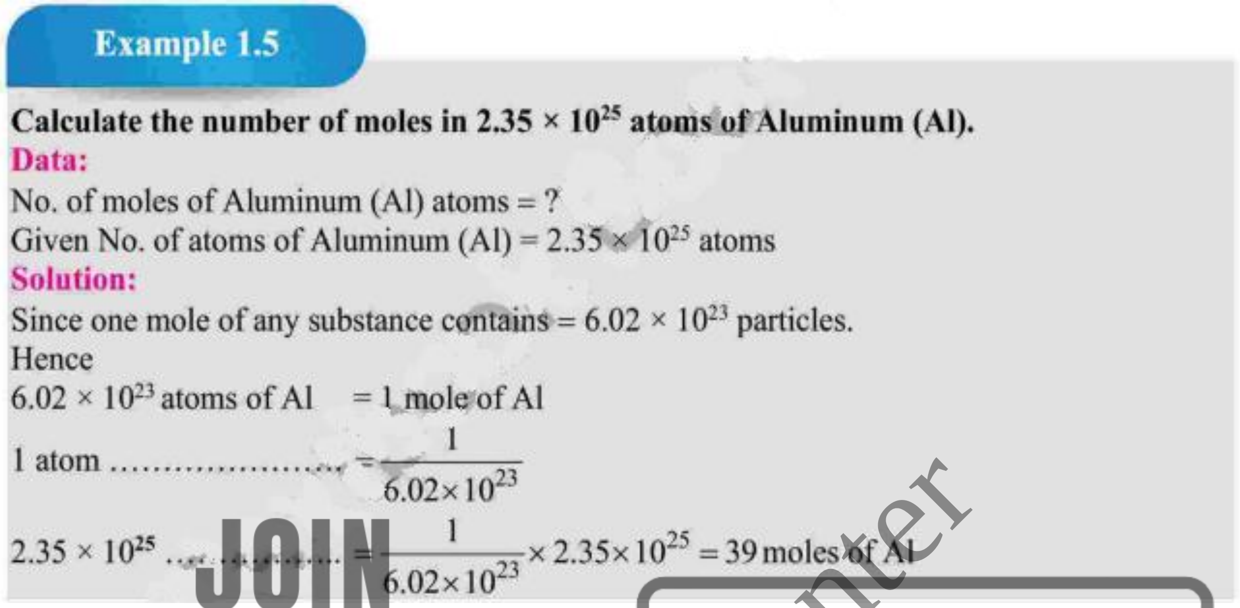
Given Molar mass of Gold (Au) = 197 g/mol

Solution:

6.02×10^{23} atoms of Gold (Au) = 197 g of Gold

1 atom ……………………… $= \frac{197}{6.02\times10^{23}}$ g of Gold

4.39×10^{22} ………………... $= \frac{197\times4.39\times10^{22}}{6.02\times10^{23}}$ =14.365 g of Gold



Example 1.5

Calculate the number of moles in 2.35×10^{25} atoms of Aluminum (Al).

Data:

No. of moles of Aluminum (Al) atoms = ?

Given No. of atoms of Aluminum (Al) = 2.35×10^{25} atoms

Solution:

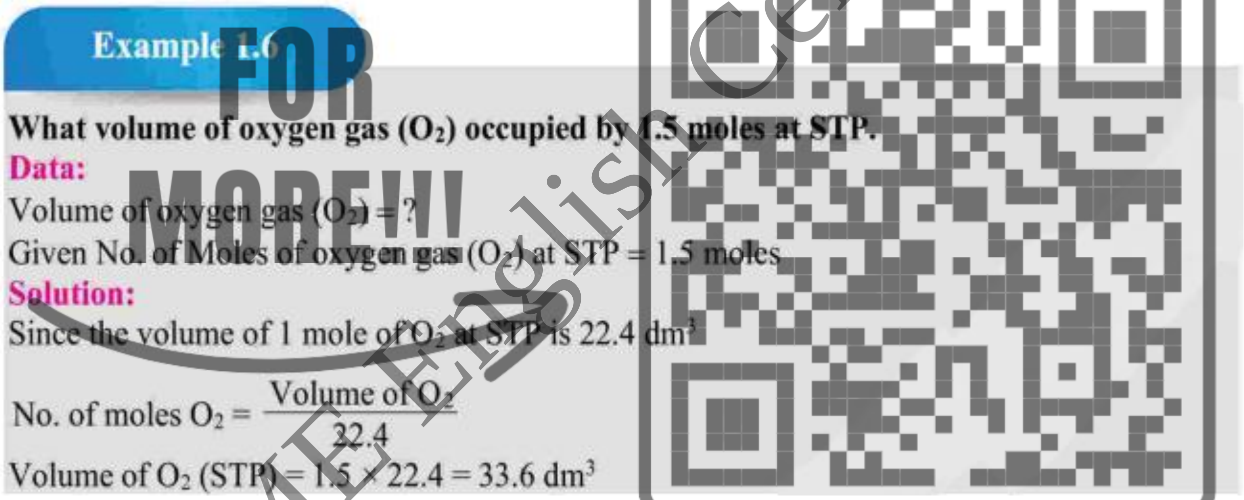
Since one mole of any substance contains = 6.02×10^{23} particles.

Hence

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

$$1 \text{ atom } \ldots\ldots\ldots\ldots = \frac{1}{6.02\times10^{23}}$$

$$2.35\times10^{25} \ldots\ldots\ldots\ldots = \frac{1}{6.02\times10^{23}}\times 2.35\times10^{25} = 39 \text{ moles of Al}$$



Example 1.6

What volume of oxygen gas (O_2) occupied by 1.5 moles at STP.

Data:

Volume of oxygen gas (O_2) = ?

Given No. of Moles of oxygen gas (O_2) at STP = 1.5 moles

Solution:

Since the volume of 1 mole of O_2 at STP is 22.4 dm^3

$$\text{No. of moles } O_2 = \frac{\text{Volume of } O_2}{22.4}$$

Volume of O_2 (STP) = $1.5 \times 22.4 = 33.6\ dm^3$

Example 1.7

Calculate mass of carbon dioxide (CO_2) that can be obtained by complete thermal decomposition of 50g Lime stone ($CaCO_3$).

$$CaCO_{3(s)} \xrightarrow{\text{Heat}} CaO_{(s)} + CO_{2(g)}$$

Data:

Mass of carbon dioxide (CO_2) =?
Given mass of Lime stone ($CaCO_3$) = 50g

Solution:

No. of moles in 50g $CaCO_3$ $= \frac{50}{100} = 0.5$ moles

1 mole of $CaCO_3$ gives .... = 1 mole of CO_2

0.5 moles .... = 0.5 moles of CO_2

Now, mass of CO_2 .... = moles of CO_2 × molar mass of CO_2

Mass of $CO_2 = 0.5 \times 44$ = 22g

Example 1.8

Mass of 49g of solid potassium chlorate ($KClO_3$) on heating decomposes completely to potassium chloride (KCl) with the liberation of oxygen gas (O_2).

$$2KClO_{3(s)} \xrightarrow{\text{Heat}} 2KCl_{(s)} + 3O_{2(g)}$$

Determine volume of oxygen gas (O_2) liberated at STP

Data:

Given mass of potassium chlorate ($KClO_3$) = 49g
Volume of oxygen gas (O_2) =?

Solution:

No. of moles of $KClO_3 = \frac{49}{122.5} = 0.4$ moles

2 moles of $KClO_3$ gives = 3 moles of O_2

1 .... $= \frac{3}{2}$ moles of O_2

0.4 ....$= \frac{3}{2} \times 0.4 = 0.6$ moles of O_2

Now the volume of O_2 at STP can be determined by using Avogadro's concept.

Volume of 1 mole of a gas at STP = $22.4dm^3$
Volume of 0.6 mole of a oxygen gas (O_2) at STP = $22.4 \times 0.6\ dm^3$
Volume of O_2 at STP = $13.44\ dm^3$

Example 1.9

Calculate the volume of carbon dioxide at STP that can be produced by the complete burning of 50 dm^3 of butane gas (C_4H_{10}) in the excess supply of oxygen gas (O_2).

$$2C_4H_{10(g)} + 13O_{2(g)} \xrightarrow{\text{Heat}} 8CO_{2\,(g)} + 10H_2O_{(g)}$$

Data:

Volume of carbon dioxide (CO_2) at STP =?

Given volume of Butane (C_4H_{10}) = 50 dm^3

Solution:

According to balanced chemical equation:

2 dm^3 of butane produces = 8 dm^3 of carbon dioxide

1 dm^3.......................... $= \frac{8}{2}$

50 dm^3 .... $= \frac{8}{2} \times 50 = 200$ dm^3 of CO_2

Example 1.10

Add 1.31×10^3 and 3.15×10^2 by using the rule of exponential notation.

Solution:

The value 3.15×10^2 is initially converted into 0.315×10^3 by placing decimal point to the left. Then add the coefficients of both values.

$$\begin{array}{r} 1.31 \times 10^3 \\ +\,0.315 \times 10^3 \\ \hline 1.625 \times 10^3 \end{array}$$

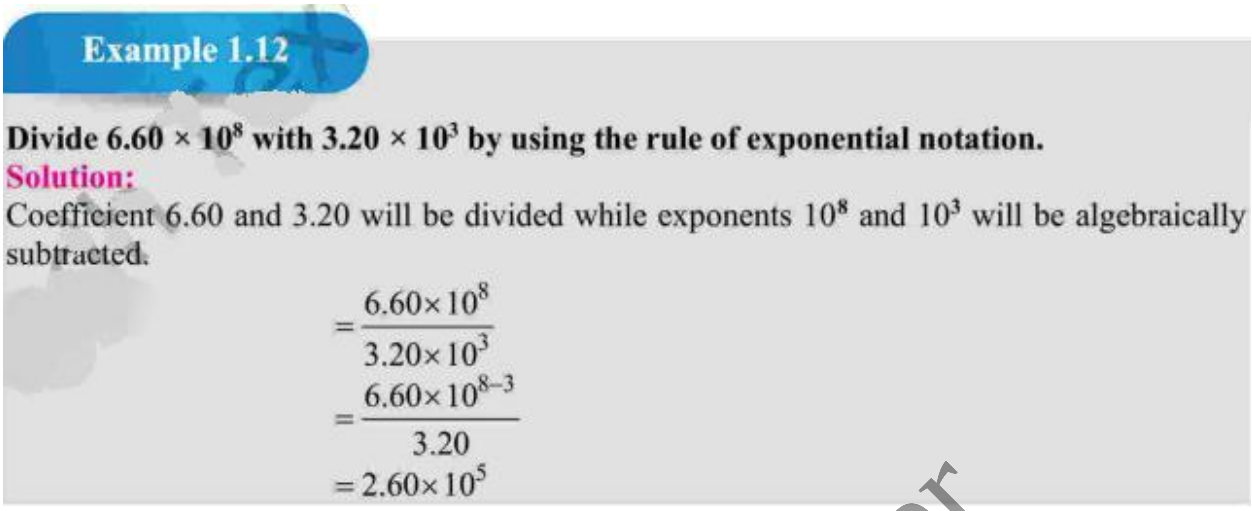
Example 1.11

Multiply 7.0×10^{12} and 2.0×10^{-3} by using the rule of exponential notation.

Solution:

Coefficients 7.0 and 2.0 will be multiplied while exponents 10^{12} and 10^{-3} will be algebraically added.

$$= (7.0)\,(2.0) \times 10^{12-3}$$
$$= 14 \times 10^9$$
$$= 1.4 \times 10^{10}$$



Example 1.12

Divide 6.60×10^8 with 3.20×10^3 by using the rule of exponential notation.

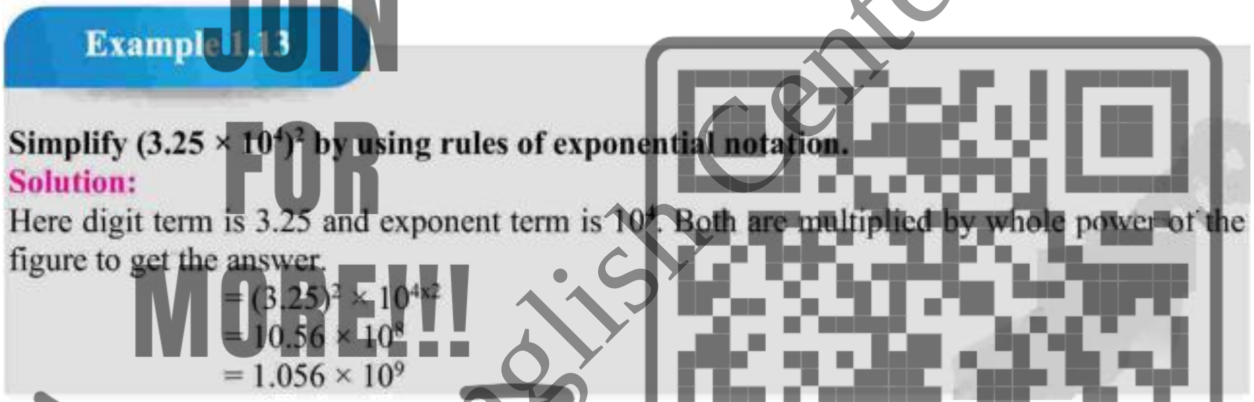
Solution:

Coefficient 6.60 and 3.20 will be divided while exponents 10^8 and 10^3 will be algebraically subtracted.

$$= \frac{6.60 \times 10^8}{3.20 \times 10^3}$$

$$= \frac{6.60 \times 10^{8-3}}{3.20}$$

$$= 2.60 \times 10^5$$



Example 1.13

Simplify $(3.25 \times 10^4)^2$ by using rules of exponential notation.

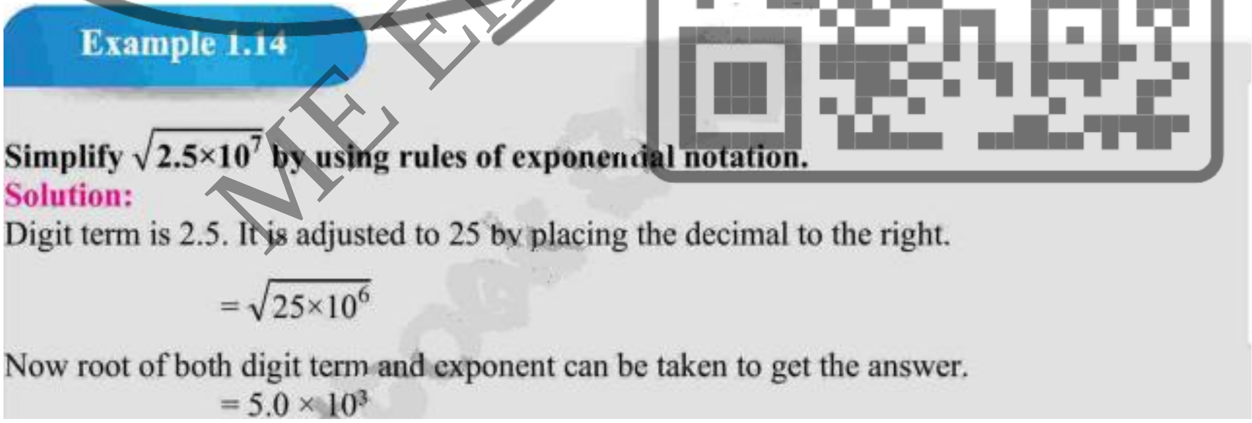
Solution:

Here digit term is 3.25 and exponent term is 10^4. Both are multiplied by whole power of the figure to get the answer.

$$= (3.25)^2 \times 10^{4 \times 2}$$

$$= 10.56 \times 10^8$$

$$= 1.056 \times 10^9$$



Example 1.14

Simplify $\sqrt{2.5 \times 10^7}$ by using rules of exponential notation.

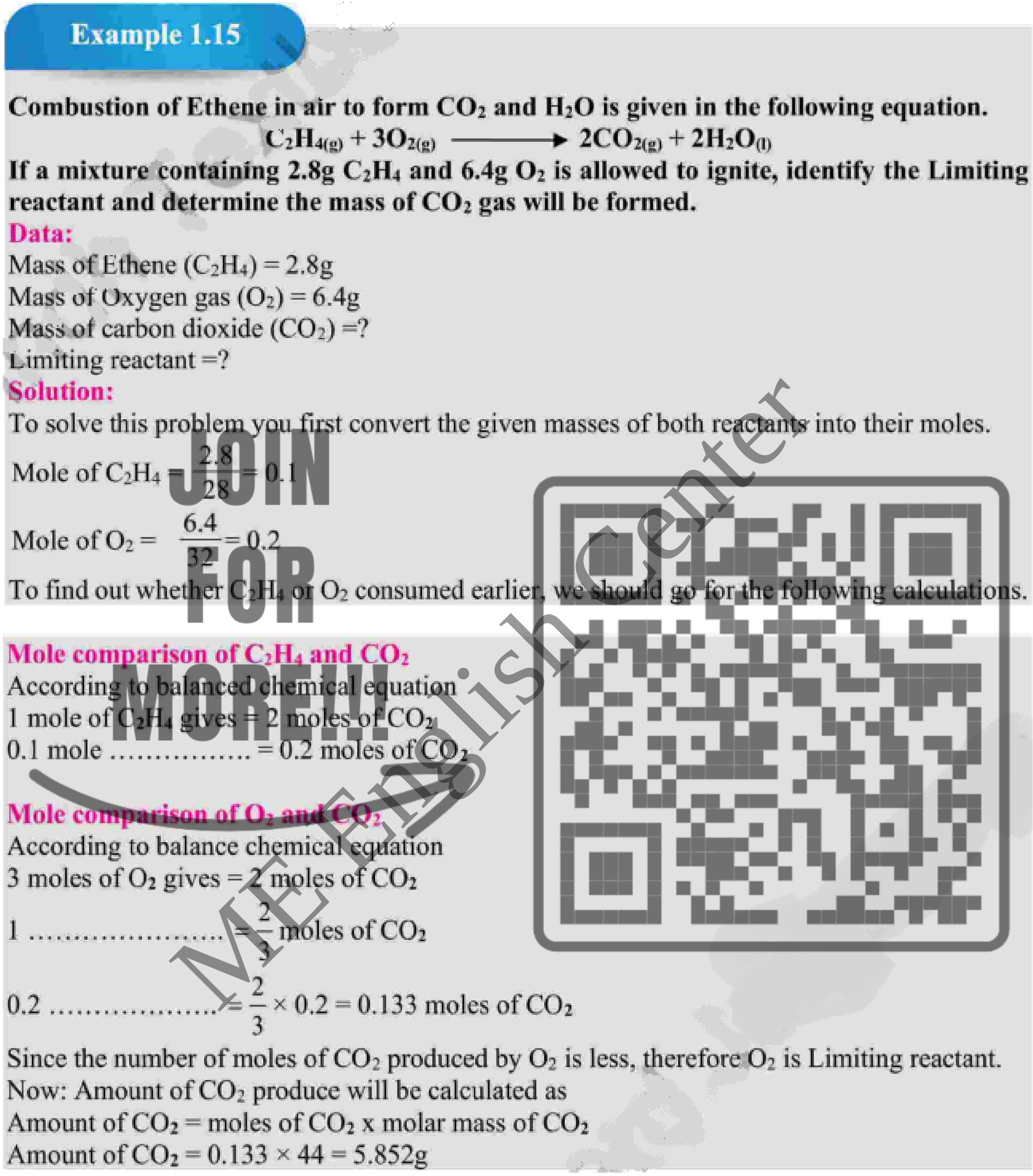
Solution:

Digit term is 2.5. It is adjusted to 25 by placing the decimal to the right.

$$= \sqrt{25 \times 10^6}$$

Now root of both digit term and exponent can be taken to get the answer.

$$= 5.0 \times 10^3$$



Example 1.15

Combustion of Ethene in air to form CO_2 and H_2O is given in the following equation.

$$C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)}$$

If a mixture containing 2.8g C_2H_4 and 6.4g O_2 is allowed to ignite, identify the Limiting reactant and determine the mass of CO_2 gas will be formed.

Data:

Mass of Ethene (C_2H_4) = 2.8g
Mass of Oxygen gas (O_2) = 6.4g
Mass of carbon dioxide (CO_2) =?
Limiting reactant =?

Solution:

To solve this problem you first convert the given masses of both reactants into their moles.

$$\text{Mole of } C_2H_4 = \frac{2.8}{28} = 0.1$$

$$\text{Mole of } O_2 = \frac{6.4}{32} = 0.2$$

To find out whether C_2H_4 or O_2 consumed earlier, we should go for the following calculations.

Mole comparison of C_2H_4 and CO_2

According to balanced chemical equation
1 mole of C_2H_4 gives = 2 moles of CO_2
0.1 mole ……………. = 0.2 moles of CO_2

Mole comparison of O_2 and CO_2

According to balance chemical equation
3 moles of O_2 gives = 2 moles of CO_2
1 ………………….. = $\frac{2}{3}$ moles of CO_2
0.2 ………………. = $\frac{2}{3} \times 0.2 = 0.133$ moles of CO_2

Since the number of moles of CO_2 produced by O_2 is less, therefore O_2 is Limiting reactant.
Now: Amount of CO_2 produce will be calculated as
Amount of CO_2 = moles of CO_2 x molar mass of CO_2
Amount of $CO_2 = 0.133 \times 44 = 5.852$g

Example 1.16

When Aluminum is heated with Nitrogen gas at 700 °C, it gives Aluminum nitride.

$$2Al_{(s)} + N_{2(g)} \longrightarrow 2AlN_{(s)}$$

If 67.5 g of Aluminum and 140g of Nitrogen gas are allowed to react, find out the:

(a) Limiting reactant?

(b) Mass of Aluminum nitride (AlN) produced?

(c) Mass of excess reactant?

(Atomic mass of Al is 27 a.m.u and N is 14 a.m.u)

Solution:

We first convert the given amount of reactants into moles.

$$Al = \frac{62.5}{27} = 2.5 \text{ moles}$$

$$N_2 = \frac{140}{28} = 5 \text{ moles}$$

Mole comparison of Al and AlN

According to balanced chemical equation

2 moles of Al gives = 2 moles of AlN

1 ………………… $= \frac{2}{2}$

2.5 ……………… $= \frac{2}{2} \times 2.5 = 2.5$ moles

Mole comparison of N_2 and AlN

1 mole of N_2 gives = 2 moles of AlN

5 moles ………… = 2 × 5 = 10 moles

Since number of moles of AlN produced by Aluminum is less, therefore Limiting reactant is Aluminum

Amount of AlN is calculated by multiplying its moles with molar mass

Mass of AlN = 2.5 × 41 = 102.5g

Now, mass of excess reactant is determined as

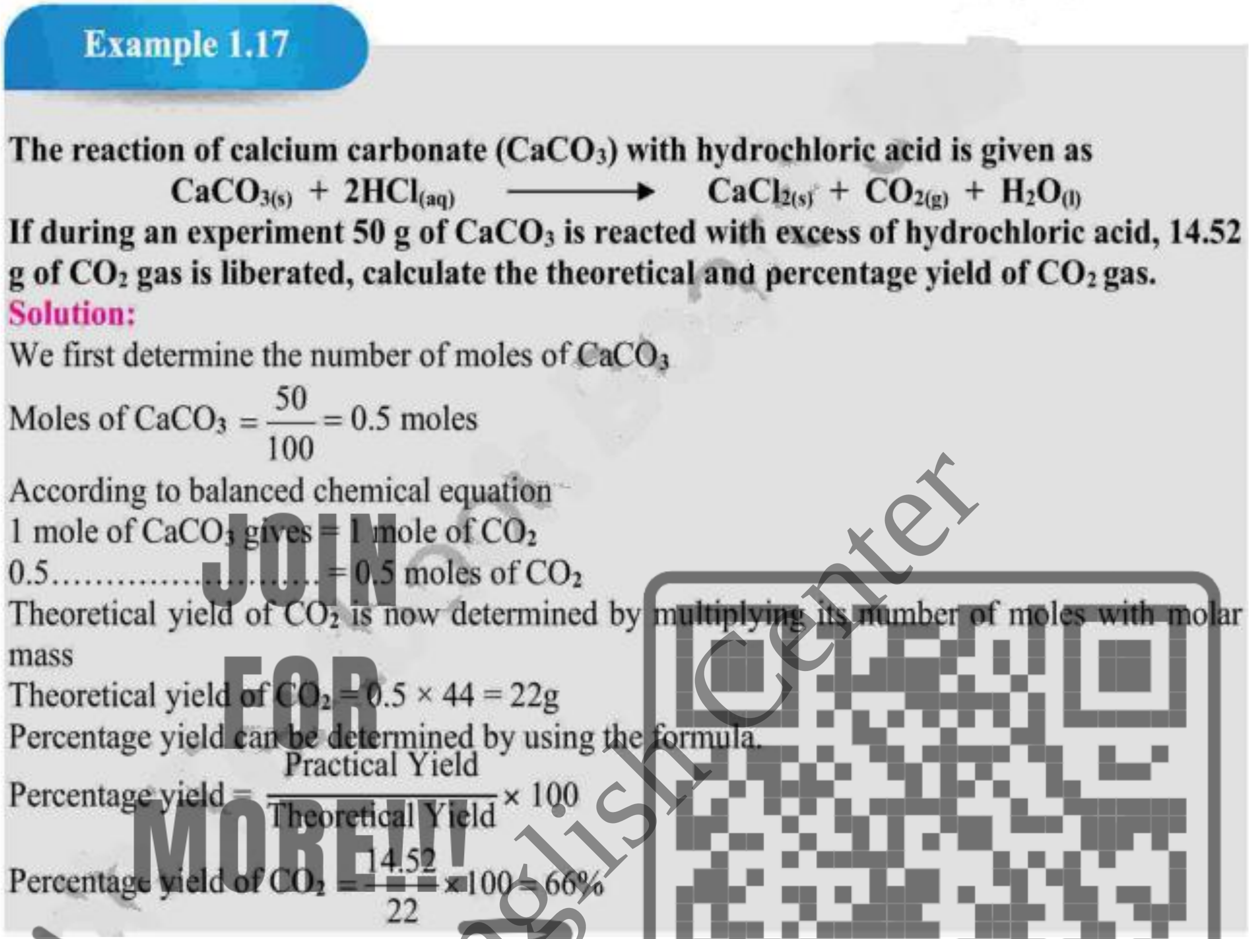
2 moles of Al combine with = 1 mole of N_2

1 ………………………… $= \frac{1}{2}$ mole of N_2

2.5 ……………………….. $= \frac{1}{2} \times 2.5 = 1.25$ moles of N_2

Excess moles of N_2 = 5 – 1.25 = 3.75moles

Excess amount of N_2 = 3.75 × 28 = 105g



Example 1.17

The reaction of calcium carbonate ($CaCO_3$) with hydrochloric acid is given as

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(s)} + CO_{2(g)} + H_2O_{(l)}$$

If during an experiment 50 g of $CaCO_3$ is reacted with excess of hydrochloric acid, 14.52 g of CO_2 gas is liberated, calculate the theoretical and percentage yield of CO_2 gas.

Solution:

We first determine the number of moles of $CaCO_3$

Moles of $CaCO_3 = \frac{50}{100} = 0.5$ moles

According to balanced chemical equation

1 mole of $CaCO_3$ gives = 1 mole of CO_2

0.5…………………… = 0.5 moles of CO_2

Theoretical yield of CO_2 is now determined by multiplying its number of moles with molar mass

Theoretical yield of $CO_2 = 0.5 \times 44 = 22g$

Percentage yield can be determined by using the formula.

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

$$\text{Percentage yield of } CO_2 = \frac{14.52}{22} \times 100 = 66\%$$

Short Questions

1. Define the following:

(i) Stoichiometry (ii) Exponential Notation (iii) Molar Volume

Ans)

(i) Stoichiometry: Stoichiometry is a branch of chemistry that deals with the quantitative relationships between the reactants and products in a chemical reaction.

(ii) Exponential Notation: Exponential notation, also known as scientific notation or standard form, is a way of representing numbers, particularly very large or very small ones, in a more concise and manageable form.

(iii) Molar Volume: Molar volume is a term used in chemistry to describe the volume occupied by one mole of any substance, typically a gas, at a specific temperature and pressure.

2. Express the following numbers in exponential notation:

(i) 3652 **(ii) 0.0231** **(iii) 0.000072**

Ans)

(i) 3.652×10^{3}

(ii) 2.31×10^{-2}

(iii) 7.2×10^{-5}

3. Express the following in simple numbers.

(i) 3.26×10^{-3} **(ii) 1.921×10^{2}** **(iii) 1.02×10^{5}**

Ans)

(i) 0.00326

(ii) 192.1

(iii) 102000

4. Define rounding of data. Give various rules of rounding of data.

Ans) **Rounding off data:** To reduce a number upto desired significant figures and adjust the last reported digit is known as rounding off data.

Rules for rounding off data:

1. If digit to be dropped is greater than 5, then add 1 to the digit to be retained.
   For example: 5.768 is rounded up to 5.77 if three significant figures are needed to be retained.
2. If digit to be dropped is less than 5, then simply drop it without changing preceding number.
   For example: if 5.734 is rounded up to three significant figures, we get 5.73
3. If digit to be dropped is exactly 5, there are two conditions:
   - If the digit to be retained is even, then just drop the 5.
     For example: when 7.865 is rounded up to three figures we get 7.86
   - If the digit to be retained is odd, then add 1 to it.
     For example: 23.35 is rounded to 23.4

Descriptive Questions

1. Define theoretical yield, actual yield and percent yield. Why the practical yield is often less than theoretical yield?

Ans) Theoretical Yield: The maximum amount of product obtained by a balanced chemical reaction by using its Limiting reactant is known as Theoretical Yield.

Practical or Actual yield: The actual amount of product which is formed in experiment is called Practical or Actual yield.

Percent yield: The ratio of practical yield to theoretical yield. This ratio is known as percent yield.

Reasons which make practical yield less than theoretical yield: The practical yield in chemical reactions is often less than the theoretical yield due to reasons such as incomplete reactions, side reactions, losses during transfer and purification, impurities, experimental errors, non-ideal conditions, product decomposition, and mass transfer limitations. These factors can result in a lower actual output of the desired product compared to what is theoretically predicted.

2. What is meant by mole and Avogadro's number? How they inter related to each other?

Ans) Mole: A mole is defined as gram atomic mass or gram molecular mass or gram formula mass of any substance (atoms, molecules, ions) which contains 6.02×10^{23} particles.

Avogadro's number (N_A): The number of particles present in one mole of any substance is called Avogadro's number (N_A) and its numerical value is 6.02×10^{23}

Relationship between Moles and Avogadro's Number: Since one mole of any substance contains Avogadro's number of entities, you can also calculate the number of entities (atoms, molecules, or ions) in a given number of moles using the formula:

$$\text{Number of Entities} = \text{Moles} \times N_A$$

For example, if you have 2 moles of oxygen (O_2), you can calculate the number of oxygen molecules in that sample as follows:

$$\text{Number of } O_2 = 2 \times 6.02 \times 10^{23} = 1.204 \times 10^{24} \text{ molecules}$$

3. What is meant by Avogadro's number? Explain concept of mole with the help of Avogadro's number.

Ans)

Avogadro's number (N_A): The number of particles present in one mole of any substance is called Avogadro's number (N_A) and its numerical value is $6.02 x 10^{23}$.

Concept of mole with the help of Avogadro's number: Avogadro's number is a constant, approximately equal to 6.02×10^{23}. It represents the number of entities (such as atoms, molecules, or ions) in one mole of a substance. In other words, one mole of any substance contains Avogadro's number of individual entities.

4. What is a Limiting reactant? How does it control the amount of product formed in a chemical reaction.

Ans) Limiting reactant: The reactant which is entirely consumed first during chemical reaction is called Limiting reactant or Limiting reagent.

The amount of product formed is limited by limiting reagent, since the reaction cannot continue without it.

For example: Consider the reaction where hydrogen gas (H_2) reacts with oxygen gas (O_2) to produce water (H_2O)

$$2H_2 + O_2 \rightarrow 2H_2O$$

In this balanced chemical equation, it's clear that 2 moles of hydrogen (H_2) react with 1 mole of oxygen (O_2) to produce 2 moles of water (H_2O).

Now, let's imagine you have the following quantities of reactants:

- 4 moles of hydrogen gas (H_2)
- 2 moles of oxygen gas (O_2)

To determine the limiting reactant, we need to calculate how many moles of water (H_2O) can be produced using each of the reactants while adhering to the stoichiometry of the balanced equation.

Using Hydrogen (H_2):

Since 2 moles of H_2 produce 2 moles of H_2O, with 4 moles of H_2, you can produce:

(4 moles H_2) x (2 moles H_2O / 2 moles H_2) = 4 moles of H_2O

Using Oxygen (O_2):

Since 1 mole of O_2 produces 2 moles of H_2O, with 2 moles of O_2, you can produce:

(2 moles O_2) x (2 moles H_2O / 1 mole O_2) = 4 moles of H_2O

Now, we can see that both reactants can theoretically produce 4 moles of water (H2O). However, the key insight here is that you have 4 moles of hydrogen and only 2 moles of oxygen. Even though both reactants can produce the same amount of product, you will run out of oxygen after 2 moles of water are produced. Therefore, oxygen is the limiting reactant in this scenario.

Thus, the amount of H_2O formed is limited by O_2, since the reaction cannot continue without O_2.

Numerical Questions

1. Calculate the number of moles and molecules in:

(i) 38g of carbon disulphide (CS_2) **(ii) 68.4g of sucrose ($C_{12}H_{22}O_{11}$)**

Data:

(i) Mass of CS_2 = 38g

No. of moles of CS_2 = ?

No. of molecules of CS_2 = ?

(ii) Mass of $C_{12}H_{22}O_{11}$ = 68.4 g

No. of moles of $C_{12}H_{22}O_{11}$ = ?

No. of molecules of $C_{12}H_{22}O_{11}$ = ?

Solution:

(i)

Moles of CS_2 = $\frac{\text{mass of } CS_2}{\text{molecular mass of } CS_2}$

Moles of CS_2 = $\frac{38}{76}$ = 0.5 moles

No. of molecules = moles of CS_2 x N_A

No. of molecules = 0.5 x 6.02 x 10^{23} = 3.01 x 10^{23} molecules

(ii) Moles of $C_{12}H_{22}O_{11}$ = $\frac{\text{mass of } C_{12}H_{22}O_{11}}{\text{molecular mass of } C_{12}H_{22}O_{11}}$

Molecular mass of $C_{12}H_{22}O_{11}$ = $\frac{68.4}{342}$ = 0.2 moles

No. of molecules = moles of $C_{12}H_{22}O_{11}$ of x N_A

No. of molecules = 0.2 x 6.02 x 10^{23} = 1.204 x 10^{23} molecules

2. Ammonia gas can be produced by heating together the solid NH_4Cl and $Ca(OH)_2$.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

If a mixture containing 100g of each of these solids is heated, determine the limiting reactant and the mass of NH_3 gas produced.

Data:

Mass of NH_4Cl = 100 g

Mass of $Ca(OH)_2$ = 100 g

Mass of NH_3 = ?

Limiting reactant =?

Solution:

To solve this problem you first convert the given masses of both reactants into their moles.

Moles of NH_4Cl = $\frac{100}{53.5}$ = 1.87 moles

Moles of $Ca(OH)_2$ = $\frac{100}{74}$ = 1.35 moles

To find out whether NH_4Cl or $Ca(OH)_2$; consumed earlier, we should go for the following calculations.

Mole comparison of NH_4Cl and NH_3:

According to balanced chemical equation

2 mole of NH_4Cl gives = 2 moles of NH_3

1 mole of NH_4Cl gives = 1 moles of NH_3

1.87 moles …………. = 1.87 moles of NH_3

Mole comparison of $Ca(OH)_2$ and NH_3:

1 mole of $Ca(OH)_2$ gives = 2 moles of NH_3

1.35 moles …………. = 2.7 moles of NH_3

Since the number of moles of NH_3 produced by NH_4Cl is less, **therefore NH_4Cl is Limiting reactant**. Now: Amount of NH_3 produced will be calculated as

Amount of NH_3 = moles of NH_3 x molar mass of NH_3

Amount of NH_3 = 1.87 x 17 = 31.79 g

3. Aluminum chloride is used in the manufacturing of rubber. It is produced by allowing Aluminum to react with Cl_2 gas at 650°C.

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(l)}$$

When 160g Aluminum reacts with excess of chlorine, 650g of $AlCl_3$ is produced. What is the percentage yield of $AlCl_3$?

Data:

Mass of Al = 160g

Mass of $AlCl_3$ = 650g

Percentage yield of $AlCl_3$ = ?

Solution:

We first determine the number of moles of Al

Moles of Al = $\frac{160}{27}$ = 5.93 moles

According to balanced chemical equation

2 mole of Al gives = 2 moles of $AlCl_3$

1 mole of Al gives = 1 moles of $AlCl_3$

5.93 moles …………. = 5.93 moles of $AlCl_3$

Theoretical yield of $AlCl_3$ is now determined by multiplying its number of moles with molar mass

Theoretical yield of $AlCl_3$ = 5.93 x 133.5 = 791.655 g

Percentage yield can be determined by using the formula.

Percentage yield = $\frac{\text{Practical Yield}}{\text{Theoretical Yield}}$ x 100

Percentage yield of $AlCl_3$ = $\frac{650}{791.655}$ x 100

Percentage yield of $AlCl_3$ = 82.1 %

4. 1.6g of a sample of gas occupies a volume of 1.12 dm^3 at STP. Determine the molar mass of the substance.

Data:

Mass of gas = 1.6 g

Volume of gas = 1.12 dm^3

Molar mass of gas = ?

Solution:

Since the volume of 1 mole of gas is 44 dm^3

No. of moles of gas = $\frac{\text{Volume of gas}}{22.4}$

No. of moles of gas = $\frac{1.12}{22.4}$ = 0.05 moles

No. of moles = $\frac{\text{mass of gas}}{\text{molecular mass of gas}}$

0.05 = $\frac{1.6}{\text{molecular mass of gas}}$

Molecular mass of gas = 32 g/mol

5. Silver sulphide (Ag_2S) is an anti microbial agent. In an experiment 24.8 g Ag_2S is reacted with the excess of hydrochloric acid as given in the following reaction.

$$Ag_2S_{(s)} + 2HCl_{(aq)} \longrightarrow 2AgCl_{(s)} + H_2S_{(g)}$$

Calculate the

(i) Mass of AgCl formed

(ii) Volume of H_2S produced at STP

(At. Mass of Ag is 108 g/mol and S is 32 g/mol)

Data:

Mass of Ag_2S = 24.8g

(i) Mass of AgCl formed = ?

(ii) Volume of H_2S produced at STP = ?

Solution:

(i) No. of moles in 24.8g of Ag_2S = $\frac{24.8}{248}$ = 0.1 moles

According to balanced chemical equation

1 mole of Ag_2S gives = 2 moles of AgCl

1 mole of Ag_2S gives = 2 moles of AgCl

0.1 moles …………. = 0.2 moles of AgCl

Moles of AgCl = $\frac{\text{mass of AgCl}}{\text{molecular mass of AgCl}}$

0.2 = $\frac{\text{mass of AgCl}}{143.5}$

Mass of AgCl = 28.7 g

(ii) According to balanced chemical equation

1 mole of Ag_2S gives = 1 moles of H_2S

0.1 moles …………. = 0.1 moles of H_2S

No. of moles of H_2S = $\frac{\text{Volume of } H_2S}{22.4}$

$0.1 = \frac{\text{Volume of } H_2S}{22.4}$

Volume of H_2S = 2.24 dm^3

6. Calculate each of the following quantities.

(i) Number of moles in 6.4g of SO_2.

Data:

Moles of SO_2 = ?

Mass of SO_2 = 6.4 g

Solution:

Moles of $SO_2 = \frac{\text{mass of } SO_2}{\text{molecular mass of } SO_2}$

Moles of $CS_2 = \frac{6.4}{64}$ = 0.1 moles

(ii) Mass in gram of 4.5 moles of ethyne (C_2H_2)

Data:

Moles of C_2H_2 = 4.5

Mass of C_2H_2 = ?

Solution:

Moles of $C_2H_2 = \frac{\text{mass of } C_2H_2}{\text{molecular mass of } C_2H_2}$

$4.5 = \frac{\text{mass of } C_2H_2}{26}$

Mass of C_2H_2 = 117 g

(iv) Volume in cm³ of 38.4g O_2 gas at STP

Data:

Mass of O2 = 38.4g

Volume in cm³ = ?

Solution:

Moles of $O_2 = \frac{\text{mass of } O_2}{\text{molecular mass of } O_2}$

Moles of $O_2 = \frac{38.4}{32}$

Moles of O_2 = 1.2 moles

No. of moles of $O_2 = \frac{\text{Volume of } O_2}{22.4}$

$1.2 = \frac{\text{Volume of } O_2}{22.4}$

Volume of O_2 = 26.88 dm^3 = 26.88 x 1000 = 26880 cm^3

(v) Number of molecules of 126g water

Data:

Number of molecules of H_2O = ?

Mass of H_2O = 126g

Solution:

Moles of $H_2O = \frac{\text{mass of } H_2O}{\text{molecular mass of } H_2O}$

Moles of $H_2O = \frac{126}{18}$

Moles of H_2O = 7 moles

Number of molecules of H_2O = Moles of H_2O x N_A

Number of molecules of H_2O = 7 x 6.02 x 10^{23}

Number of molecules of H_2O = 42.14 x 10^{23} molecules

(vi) Mass in gram of 4.8 x 10^{24} atoms of sodium.

Data:

No. of atoms = 4.8 x 10^{24} atoms

Mass of Na = ?

Solution:

No. of atoms = moles of Na x N_A

4.8 x 10^{24} = moles of Na x 6.02 x 10^{23}

Moles of Na = 7.973 moles

Moles of Na = $\frac{\text{mass of Na}}{\text{molecular mass of Na}}$

7.973 = $\frac{\text{mass of Na}}{23}$

Mass of Na = 183.379 g

(vi) Number of formula units in 333g of $CaCl_2$

Data:

Mass of $CaCl_2$ = 333g

No. of formula units = ?

Solution:

Moles of $CaCl_2$ = $\frac{\text{mass of } CaCl_2}{\text{molecular mass of } CaCl_2}$

Moles of $CaCl_2$ = $\frac{333}{111}$ = 3 moles

No. formula units of $CaCl_2$ = Moles of $CaCl_2$ x N_A

No. formula units of $CaCl_2$ = 3 x 6.02 x 10^{23}

No. formula units of $CaCl_2$ = 18.06 x 10^{23} formula units

Chapter 2: ATOMIC STRUCTURE

Multiple Choice Questions

1. Choose the correct answer

(i) Bohr's theory is not applicable to which of the following species.

(a) H (b) H^+ (c) He^{+1} (d) Li^{+2}

(ii) Nitrogen has the electronic configuration $1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^1_z$ and not $1s^2\ 2s^2\ 2p^2_x\ 2p^1_y$.This is determined by.

(a) Aufbau principle (b) Pauli's rule (c) Hund's rule (d) n+ ℓ rule

(iii) Quantum number values for 3s orbital are

(a) n=0, ℓ =1 (b) n=1, ℓ =0 (c) n=3, ℓ =1 (d) n=3, ℓ =0

(iv) The radius of first orbit of hydrogen atom is.....

(a) 529 Å (b) 52.9 Å (c) 5.29 Å (d) 0.529 Å

(v) Line spectrum is used as a tool for the identification of....

(a) Colors (b) Electrons (c) Elements (d) Molecules

(vi) In 1935 A.D. James Chadwick was awarded Nobel Prize because...

(a) He discovered proton

(b) He discovered neutron

(c) He determined the radius of hydrogen atom

(d) He gave the rules for electronic configuration

(vii) When 4d orbital is filled, the next electron enter into

(a) 5s (b) 5p (c) 5d (d) 6s

(viii) Which of the following is not an iso electronic pair

(a) Na^+ and Ne (b) Na^+ and F^- (c) Na and Ca (d) Na^+ and Mg^{+2}

(ix) Balmer series appears in the hydrogen spectrum if electron jump from any appropriate higher energy orbit to

(a) Second orbit (b) Third orbit (c) Fourth orbit (d) Fifth orbit

(x) The shape of orbital for which ℓ =0 is

(a) Spherical (b) Dumbbell (c) Double dumbbell (d) Complicated

KEY:

i. b	ii. c	iii. d	iv. d	v. c
vi. b	vii. b	viii. c	ix. a	x. a

Example 2.1

Find the radius of 4th orbit of electron in Hydrogen atom.

Solution:

The radius of n = 4 for hydrogen atom can be determined by using Bohr's equation.

$$r = \frac{a^{o}n^{2}}{Z}$$

But for hydrogen Z = 1 hence

$$r = \frac{0.529 \times (4)^{2}}{1}$$

$$r = 8.46\text{Å}$$

Calculation of Energy of electron in nth orbit:

In any orbit of an atom, the total energy of an electron is the sum of potential energy (P.E) and kinetic energy (K.E).

$$E_{total} = K.E + P.E$$

P.E is the work done in bringing the electron from infinity to a point at a distance **r** from the nucleus and can be calculated as.

$$P\cdot E = \text{work done} = -\text{ force} \times \text{ displacement}$$

$$P\cdot E = \frac{-Ze^{2}}{4\pi\varepsilon_{o}r^{2}} \times r$$

$$P\cdot E = \frac{-Ze^{2}}{4\pi\varepsilon_{o}r}$$

Here negative sign indicates that P.E decreases when electron is brought from infinity to a point at a distance **r**.

Now total energy of electron is written as

$$E_{total} = \left(\frac{1}{2}mv^{2}\right) + \left(-\frac{Ze^{2}}{4\pi\varepsilon_{o}r}\right)$$

$$E = \left[\frac{1}{2}mv^{2}\right] - \left[\frac{Ze^{2}}{4\pi\varepsilon_{o}r}\right] \text{------------ (v)}$$

The value of mv² is taken from eq(i) and insert in eq(v)

$$E = \frac{1}{2}\left[\frac{Ze^{2}}{4\pi\varepsilon_{o}r}\right] - \left[\frac{Ze^{2}}{4\pi\varepsilon_{o}r}\right]$$

$$E = \frac{-Ze^{2}}{8\pi\varepsilon_{o}r} \text{------------ (vi)}$$

Taking the value of **r** from equation (iii) and put in equation (vi)

Example 2.2

Calculate the energy of an electron in L-shell of hydrogen atom (the value of K is 2.178×10^{-18} J/atom)

Solution:

L-shell correspond to second energy level (n = 2), Bohr's formula for energy of electron is given as

$$E=\frac{-K}{n^2}$$

$$E=\frac{-2.18\times10^{-18}}{(2)^2}$$

$$E=-5.43\times10^{-19}\text{ joule}$$

Example 2.3

Calculate the wave numbers of photon when electron of a hydrogen atom jumps from 4th orbit to 2nd orbit (value of $R_H = 1.09678\times10^7\ m^{-1}$).

Solution:

$n_1 = 2$

$n_2 = 4$

$Z = 1$

$\bar{V} = ?$

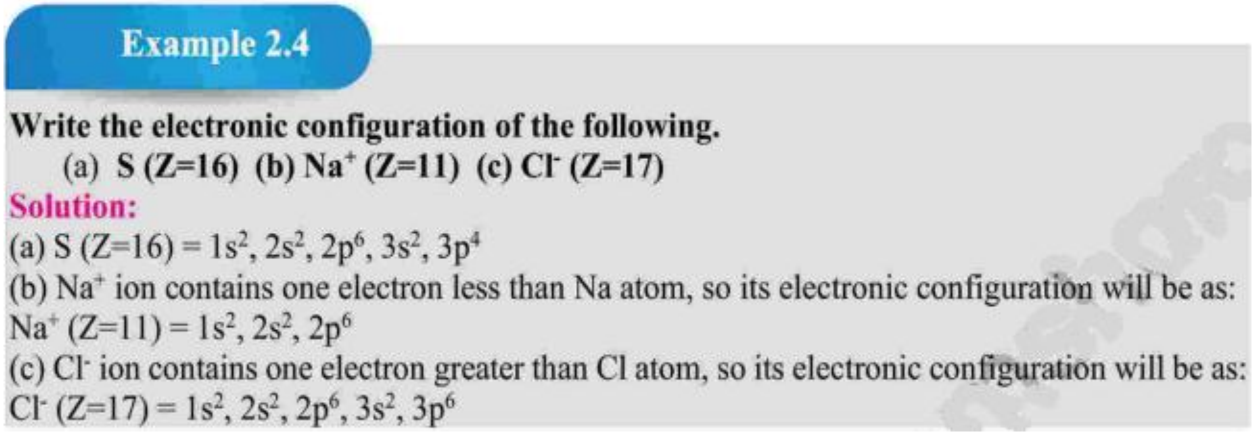
Bohr's equation for wave number of photon is given as

$$\bar{V}=R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$\bar{V}=\left(1.09678\times10^7\right)\left[\frac{1}{(2)^2}-\frac{1}{(4)^2}\right]$$

$$\bar{V}=\left(1.09678\times10^7\right)\times0.187$$

$$\bar{V}=2.051\times10^6\,m^{-1}$$



Example 2.4

Write the electronic configuration of the following.

(a) S (Z=16) (b) Na^+ (Z=11) (c) Cl^- (Z=17)

Solution:

(a) S (Z=16) = $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

(b) Na^+ ion contains one electron less than Na atom, so its electronic configuration will be as:

Na^+ (Z=11) = $1s^2, 2s^2, 2p^6$

(c) Cl^- ion contains one electron greater than Cl atom, so its electronic configuration will be as:

Cl^- (Z=17) = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

Short Questions

1. Differentiate between Continuous and Line spectrum.

Ans)

Characteristic	Continuous Spectrum	Line Spectrum
Nature of Spectrum	Continuous and uninterrupted distribution of all wavelengths within a range.	Discrete and distinct lines or bands of specific wavelengths.
Source	Hot, dense, and opaque solids, liquids, or dense gases.	Atoms or molecules undergoing energy transitions.
Production	Result of thermal emission, where atoms or molecules continuously absorb and emit photons across a wide range of wavelengths.	Result of discrete energy transitions of electrons within atoms or molecules.
Appearance	No distinct lines or gaps in the spectrum; all wavelengths are present.	Consists of individual lines or bands of specific wavelengths.
Examples	Incandescent light bulbs, stars, heated filaments, and continuous spectra from solids and liquids.	Gases in discharge tubes (e.g., hydrogen discharge tube), absorption lines in the spectra of stars, and emission spectra from excited gases.

2. Give three properties of each α , β and γ rays.

Ans)

Property	Alpha (α)	Beta (β)	Gamma (γ)
Mass	4 amu	1/1836 amu	Zero
Composition	α particle is composed of two proton and two neutron like the composition of Helium nuclei.	Beta particle is composed of electrons.	These are electromagnetic radiations.
Deflection	They are deflected by electric and magnetic fields	They are deflected by electric and magnetic fields but to the opposite direction of α – rays.	They pass without any deflection in electric and magnetic field.

3. What is the shape of orbitals for which ℓ = 0 and ℓ = 1.

Ans) The shape of orbital for which ℓ = 0 is spherical.

The shape of orbital for which ℓ = 1 is dumb-bell.

4. How does an orbital different from orbit?

Ans) An **orbit** is a concept from early atomic models like the Bohr model, suggesting that electrons move in fixed paths around the nucleus.

An **orbital**, on the other hand, is a concept from quantum mechanics and represents the three-dimensional space where there is a high probability of finding an electron with a specific energy. Orbitals are not fixed paths but describe the electron's probable location based on its wave-like behavior and are defined by quantum numbers.

5. Explain why the filling of electron in 4s orbital takes place prior to 3d?

Ans) The filling of the 4s orbital before the 3d orbital occurs because of the Aufbau Principle, which dictates that electrons fill orbitals in order of increasing energy. The 4s orbital has a lower energy level than the 3d orbitals due to its principal quantum number (n), making it closer to the nucleus. Consequently, even though the 3d orbitals precede the 4s orbital in the periodic table, the 4s orbital is filled first because it has lower energy.

6. Mention the defects of Bohr's atomic model.

Ans)

The defects of Bohr's theory or Bohr's atomic Model:

1. Bohr's model is only applicable to Hydrogen and those species which have single revolving electron around the nucleus (He^+, Li^{2+}, Be^{3+}). It could not explain the spectra of multi electrons systems like He, Li, Be, B etc.
2. According to Bohr's concept, electron revolves around nucleus in circular orbits. Later on, it was proved that electron did not move in single plane but in three dimensional spaces.
3. According to Bohr's concept, the electron in an atom is located at a definite distance from the nucleus and revolves with a definite velocity which is against the Heisenberg uncertainty principle.
4. Bohr's theory explain only the particle nature of electron and did not explain the wave nature of electron (de Broglie's hypothesis).

7. Write down the electronic configuration of the following

(i) Fe (Z=26), **(ii) Br^- (Z=35),** **(iii) Ca^{+2} (Z=20)**

Ans)

(i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
(iii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

Descriptive Questions

1. (a) State the postulates of Bohr atomic theory.

(b) Drive an expression for the frequency of radiation emitted from an electron. Given that

$$E = \frac{-me^4}{8\varepsilon_o^2 h^2 n^2}$$

Ans)

(a) Postulates of Bohr's theory:
Postulates of Bohr's theory are given below.

1. Electrons revolve around the nucleus in circular orbits situated at fixed distance from nucleus with definite energy.
2. As long as electron remains in an appropriate orbit, it neither loses, nor gains energy. Hence each orbit has a fixed energy level, however the energy of orbits increases with the increased distance from nuclei.
3. During excitation, electron absorbs some quantized energy and jump from a lower energy orbit to an appropriate higher energy orbit but when it returns back to lower energy orbit it emits quantized energy.

   $$\Delta E = E_2 - E_1 = h\nu$$

   Here 'ν' is frequency of radiation and "h" is plank constant.
4. Electron can move only in those orbits in which the angular momentum of electron (mvr) is integral multiple of nh/2π

   $$\frac{nh}{2\pi}$$

   Here 'm' and 'v' are the mass and velocity of electron and 'r' is the radius of orbit.

(b) Calculation of Energy of electron in nth orbit:

In any orbit of an atom, the total energy of an electron is the sum of potential energy (P.E) and kinetic energy (K.E).

$$E_{total} = K.E. + P.E.$$

P.E is the work done in bringing the electron from infinity to a point at a distance r from the nucleus and can be calculated as.

$$P.E = \text{work done} = -\text{force} \times \text{displacement}$$

$$P.E = \frac{-Ze^2}{4\pi\varepsilon_o r^2} \times r$$

$$P.E = \frac{-Ze^2}{4\pi\varepsilon_o r}$$

Here negative sign indicates that P.E decreases when electron is brought from infinity to a point at a distance **r**.

Now total energy of electron is written as

$$E_{total} = (\frac{1}{2}mv^2) + (-\frac{Ze^2}{4\pi\varepsilon_o r})$$

$$E = (\frac{1}{2}mv^2) - (\frac{Ze^2}{4\pi\varepsilon_o r})$$

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

$$E = \frac{1}{2}(\frac{Ze^2}{4\pi\varepsilon_o r}) - (\frac{Ze^2}{4\pi\varepsilon_o r})$$

$$E = \frac{-Ze^2}{8\pi\varepsilon_o r}$$

Since $$r = \frac{\varepsilon_o n^2 h^2}{Z\pi m e^2}$$

$$E = \frac{-Ze^2}{8\pi\varepsilon_o} \times \frac{Z\pi m e^2}{\varepsilon_o n^2 h^2}$$

$$E = \frac{-mZ^2e^4}{8\pi\varepsilon_o{}^2 n^2 h^2}$$

But for hydrogen atom, Z = 1, thus

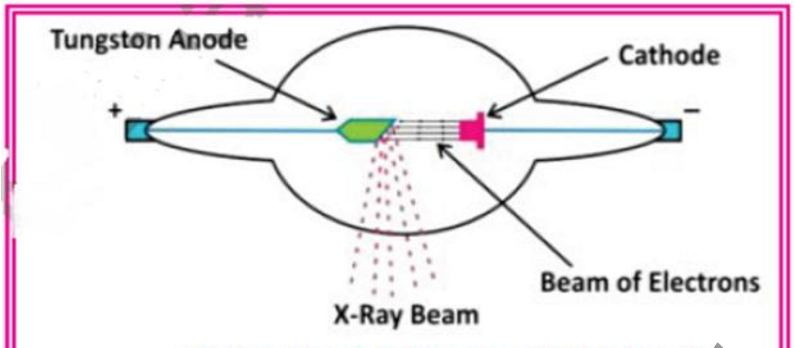
$$E = \frac{-me^4}{8\varepsilon_o{}^2 h^2}(\frac{1}{n^2})$$

2. What are X-rays? How are they produced? Give their properties and uses.

Ans) X-Rays:

Definition: An electromagnetic wave of high energy and very short wavelength, which is able to pass through many materials opaque to light.

Production of X-rays: X-rays can be produced in a special type of discharge tube in which cathode is a heated filament. Under high voltage (5000 volt) and very low pressure (0.001mm) cathode rays are emitted from cathode and travel towards anode where they strike with high speed. The transition of electron occurs in the anode atoms which cause the production of X-rays photon.



Production of X-rays in a discharge tube

Properties of X-rays:

1. These are short wave length and high energy invisible electromagnetic radiations.
2. The range of wavelength lies between 0.1-10Å.
3. They travel with the speed of light.
4. Penetration power increases as energy of x-rays increases.
5. Like cathode rays, X-rays travel in straight line.
6. These rays are unaffected by electric or magnetic field.
7. They affect the photographic film.
8. X-rays possess enough energy to ionize gases, they damage and destroy the living cells.

Uses of X-rays:

1. These are used for the analysis of metallic substance or bullets in flesh.
2. Dentists use them to examine the defective or damaged teeth.
3. These are used for destroying the cancer cells.
4. At air ports, these are used for checking the baggage containing metallic knife, blade or weapons, transport of illegal goods etc.
5. In crystallography, these are used for the determination of structures of crystals. Thus, x-ray diffraction technique was developed.

3. State and illustrate the following rules of electronic configuration.

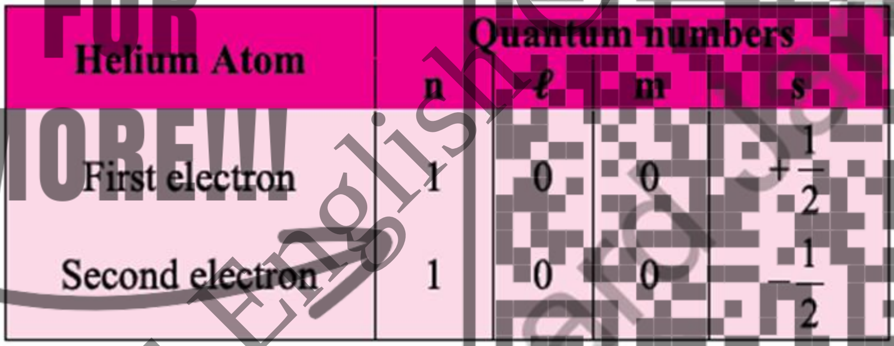
a) Pauli's exclusion rule **b) Hund's rule of maximum multiplicity**

Ans)

(a) Paul's Exclusion Principle:

Definition: In an orbital of an atom, no two electrons can have the same set of four quantum numbers, at least one quantum number must be different.

Illustration: According to this principle, two electrons in an orbital may have same values of three quantum numbers (n, ℓ, m) but the value of fourth quantum number (s) must be different. It means that if one electron of same orbital has clockwise spin then second electron must have anti-clockwise spin. Consider two electrons of helium which are lying in s-orbital of first shell ($1s^2$). The set of four quantum numbers will be written as:

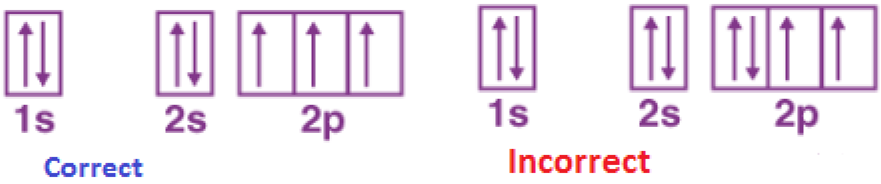


Helium Atom	Quantum numbers			
	n	ℓ	m	s
First electron	1	0	0	$+\frac{1}{2}$
Second electron	1	0	0	$-\frac{1}{2}$

(b) Hund's rule of Maximum Multiplicity:

Statement: In available degenerated orbitals (p, d and f), electrons are distributed in such a way that maximum number of half filled orbitals (single electron in orbital) are obtained.

Example: If we have three electrons to fill the 2px, 2py, 2pz orbitals, we will fill single electron in each orbital $2px^1, 2py^1, 2pz^1$ rather than double electrons $2px^{1\downarrow}, 2py^1, 2pz$.



4. Explain hydrogen spectrum in term of Bohr's theory.

Ans) Hydrogen Spectrum: Hydrogen is a simplest atom. It has one electron revolving around mono positively charged nucleus. According to Bohr's theory, at ordinary temperature the electron in hydrogen atom resides in lowest energy level i.e. in first orbit (ground state). When electric discharge is passed through hydrogen (Crook's tube) molecular hydrogen breaks up into atomic state. These atoms absorb energy from electric spark and come into excited state. Different electrons of different hydrogen atoms absorb different amount of energy and migrate to an appropriate different high energy levels (excited states). When electrons begin to revolve in higher energy level, hydrogen atoms become unstable. Then, electrons fall back to the original first orbit directly or to some other level by the emission of energies (photons). The emitted energies are equal to the difference of energies between the two levels. These radiations when pass through prism, a line emission spectrum of hydrogen is obtained. When hydrogen spectrum is viewed through high resolution spectrometer, several sharp fine lines are seen in the spectrum. The wavelengths of these lines lie into the ultraviolet, visible and infrared regions. These spectral lines are classified into five spectral series and named after their discoverers.

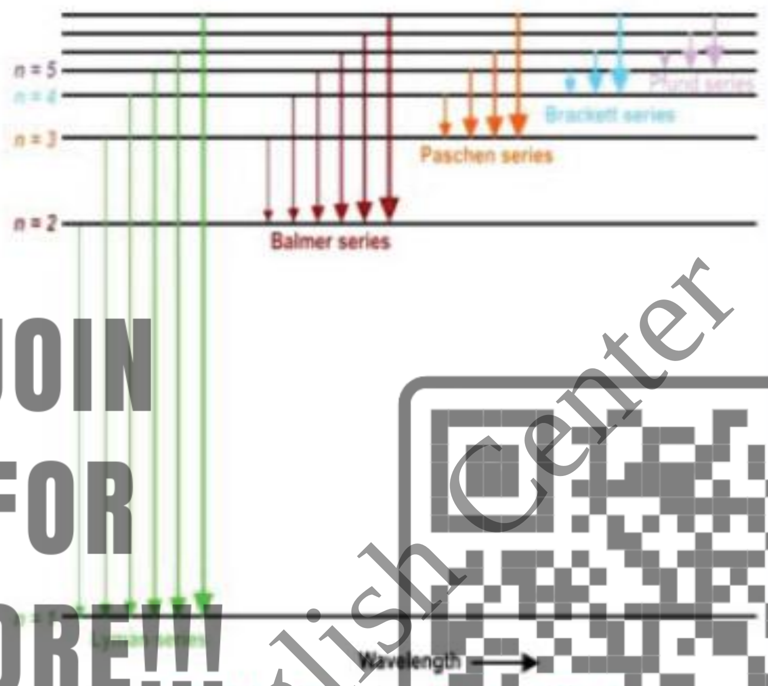
Lyman Series: These spectral lines are produced when electrons fall back from $n_2 = 2, 3, 4, 5, 6, 7 \ldots \infty$ to $n_1 = 1$ level. The range of wave number of this series lie in the ultraviolet region of the hydrogen spectrum (wave length less than 4000 Å).

Balmer Series: This series includes the spectral lines emitted by the transition of electrons occur from $n_2 = 3, 4, 5, 6, 7, \ldots \infty$ to $n = 2$ level. All the wave numbers of this series are in the visible region (wave length 4000-7000 Å).

Paschen Series: In this series, transition of electron takes place from $n_2 = 4, 5, 6, 7 \ldots \infty$ to $n_1 = 3$ level. The wave number values of these spectral lines lie in near infrared region (wave length above 7000 Å).

Bracket Series: If the migration of electrons occur from $n_2 = 5, 6, 7, 8 \ldots \infty$ to $n_1 = 4$ level Bracket series is obtained. The wave number values of these spectral lines lie in mid infrared region.

P-fund Series: These spectral lines are produced when electrons fall back from n_2 = 6, 7... to n_1=5 level. The wave number values of these spectral lines lie in far infrared region.



Origin of spectral lines of hydrogen spectrum as described by Bohr

5. Describe four quantum numbers needed to specify an electron in an atom. Write all possible values of ℓ, m and s for n = 2.

Ans) Quantum Numbers:

There are four quantum numbers.

1. Principal quantum number
2. Azimuthal quantum number
3. Magnetic quantum number
4. Spin quantum number

Principal quantum number:

Definition: Principal quantum number describes the size and energy of orbit and the distance of electron from the nucleus.

Representation: It is represented by (n).

Value: It has any positive value: 1, 2 ,3...... ∞

Formulae: The maximum number of orbitals in an orbit can be calculated by the formula n^2 and the maximum number of electrons in an orbit is determined by using the formula $2n^2$.

Azimuthal quantum number/ subsidiary quantum number:

Definition: Azimuthal quantum number is also known as subsidiary quantum number. It governs the shape of orbitals.

Representation: It is denoted by (ℓ).

Value: This can have values ℓ = 0 to (n-1). When value of ℓ = 0, the orbitals is called **s** orbital, when ℓ = 1, it is **p** orbitals, when ℓ =2, **d** orbitals and ℓ = 3, it is **f** orbital.

Formulae: The maximum number of orbitals in an orbit are determined by the formula **(2+1)** whereas maximum number of electrons in a given sub-shell are calculated by **2(2 + 1)**.

Magnetic quantum number:

Definition: It tells about the different orientations or directions of an orbital in space when subjected to magnetic field. Orbitals of same sub-shell have different orientation but same energy (degenerated orbitals) and same shapes.

Representation: It is denoted by (m).

Value: The value of **m** depends upon the values of (ℓ).

Sub-shell	(2 ℓ+1) value	Orientations (m= - ℓ to 0 to +ℓ)
s	One	1
p	Three	(-1, 0,+1)
d	Five	(-2,-1, 0, +1, +2)
f	Seven	(-3,-2.-1, 0, +1, +2, +3)

Spin quantum number:

Definition: An electron while moving in an orbital around the nucleus also rotates or spins about its own axis. The spinning of an electron is either in clock-wise or anti clock wise. This spinning of electron is associated with magnetic field.

Representation: It is denoted by (s).

Value: For clockwise spin value of spin quantum number is (-1/2) and for anti-clockwise spin value is (+1/2)

For the principal quantum number (n) equal to 2 in quantum mechanics:

1. ℓ (Azimuthal Quantum Number) can have values of 0 or 1.
    - ℓ = 0 corresponds to an s orbital.
    - ℓ = 1 corresponds to a p orbital.
2. m (Magnetic Quantum Number) can vary within the range of -ℓ to ℓ, including 0.
    - For s orbitals (ℓ = 0), m = 0.
    - For p orbitals (ℓ = 1), m can be -1, 0, or 1.
3. s (Spin Quantum Number) can be either +1/2 (spin-up) or -1/2 (spin-down).
    - These values represent the two possible electron spin states.

Numerical Questions

1. Calculate the radius of hydrogen in 3rd orbit (Bohr constant for hydrogen is 0.529 Å).

Data:

$r = ?$

$n = 3$

$a^o = 0.529$ Å

Solution:

$$r = \frac{a^o n^2}{Z}$$

$$r = \frac{0.529 \times 3^2}{1}$$

$$\mathbf{r = 4.761\ \text{Å}}$$

2. A photon of wave number 23 x 10^5 m^{-1} is emitted when electron undergoes a transition from a higher energy orbit to n = 2. Determine the orbit from which electron fall and also the spectral line appears in this transition of electron. (The value of Rydberg constant is 1.09678 x 10^7 m^{-1})

Data:

$\bar{V} = 23 \times 10^5\ m^{-1}$

$n_2 = 2$

$n_1 = ?$

No. of spectral lines from n_1 to n_2 = ?

$R_H = 1.09678 \times 10^7\ m^{-1}$

Solution:

$$\bar{V} = R_H \left[\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right]$$

$$23 \times 10^5 = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{{n_2}^2}\right]$$

$n_2 = 4.98$

But

$n_2 = 5$

No. of spectral lines from n_1 to n_2 = $\frac{(n_2-n_1)(n_2-n_1+1)}{2}$

No. of spectral lines from n_1 to n_2 = $\frac{(5-2)(5-2+1)}{2}$ = 6

Chapter#3: THEORIES OF COVALENT BONDING AND SHAPES OF MOLECULES

Multiple Choice Question

1. Choose the correct answer

(i) If the bond angle in AB_2 type molecule is 104.5°, it geometry should be:

(a) Linear (b) Pyramidal (c) Bent (d) Planar Trigonal

(ii) The highest bond energy in the following is:

(a) Cl-Cl (b) H-F (c) H-O (d) H-N

(iii) The molecule which has zero dipole moment is:

(a) NH_3 (b) HCl (c) H_2O (d) CCL_4

(iv) The molecule which has maximum bond angle:

(a) CS_2 (b) H_2O (c) NH_3 (d) BF_3

(v) The shape and hybridization of BCl_3 molecule is:

(a) Tetrahedral and sp^3 (b) Linear and sp

(c) Planar trigonal and sp^2 (d) Angular and sp^3

(vi) Amongst the following molecules which one has trigonal pyramidal shape?

(a) SO_2 (b) CO_2 (c) NH_3 (d) C_2H_4

(vii) A simple covalent molecule possesses two bond pairs and two lone pairs around the central atom, its shape should be:

(a) Linear (b) Planar trigonal (c) Angular (d) Tetrahedral

(viii) The correct relation between Debye and coulomb meter is:

(a) 1 D = 3.33 10^{-30} Cm (b) 1 D = 1.6 x 10^{-19} Cm (c) 1 D = 1.88 x 10^{-12} Cm (d) 1 D = 1.23 10^{-8} Cm

(ix) The bond order of N_2 molecule is:

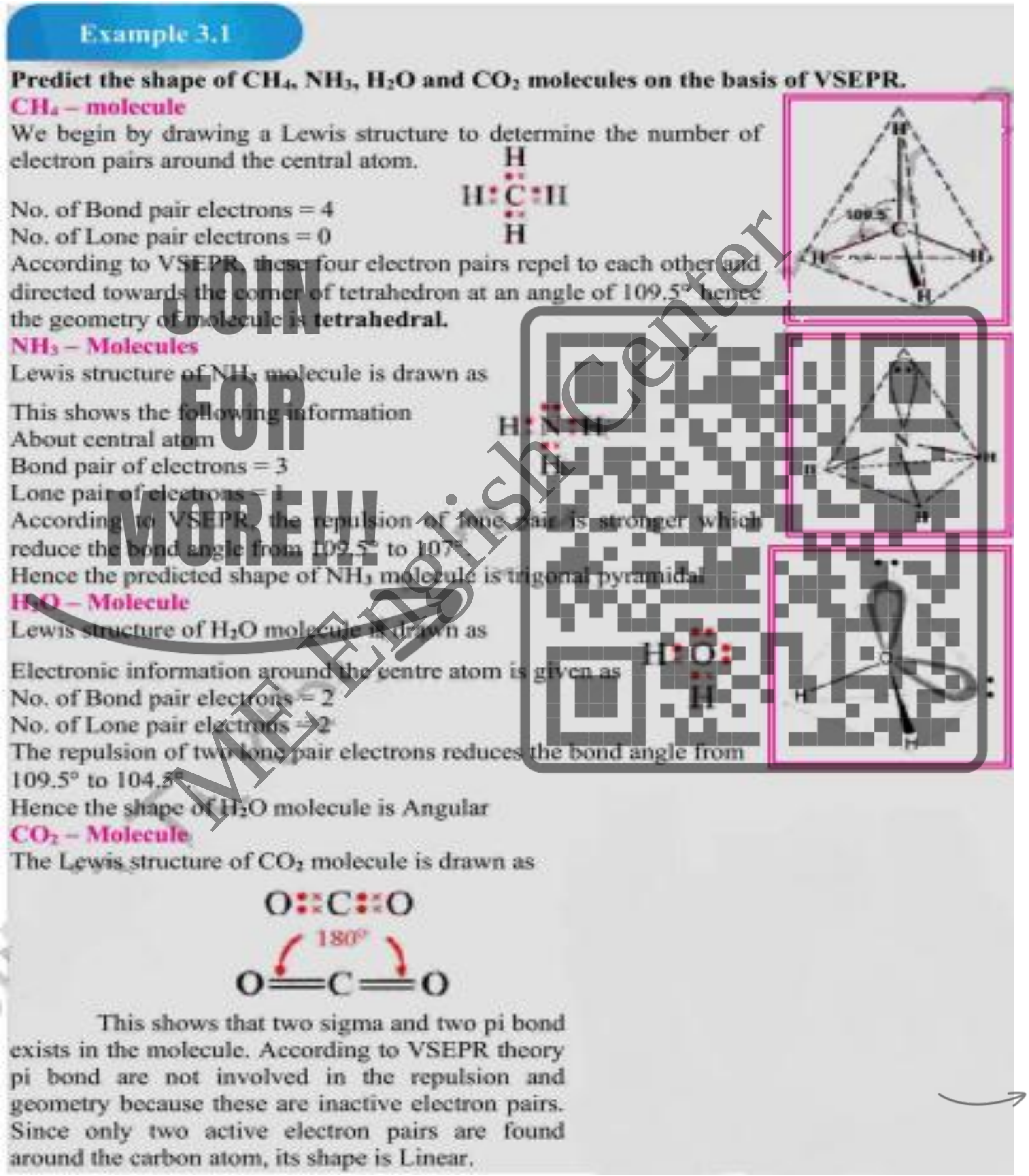
(a) 0 (b) 1 (c) 2 (d) 3

(x) The number of sigma and pi bonds in CH_4 molecule are respectively:

(a) 3 and 1 (b) 2 and 2 (c) 5 and 1 (d) 4 and 2

Key:

i. c	ii. b	iii. d	iv. a	v. c
vi. c	vii. c	viii. a	ix. d	x. c



Example 3.1

Predict the shape of CH_4, NH_3, H_2O and CO_2 molecules on the basis of VSEPR.

CH_4 – molecule

We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.

No. of Bond pair electrons = 4
No. of Lone pair electrons = 0

According to VSEPR, these four electron pairs repel to each other and directed towards the corner of tetrahedron at an angle of 109.5° hence the geometry of molecule is **tetrahedral.**

NH_3 – Molecules

Lewis structure of NH_3 molecule is drawn as

This shows the following information
About central atom
Bond pair of electrons = 3
Lone pair of electrons = 1

According to VSEPR, the repulsion of lone pair is stronger which reduce the bond angle from 109.5° to 107°.
Hence the predicted shape of NH_3 molecule is trigonal pyramidal

H_2O – Molecule

Lewis structure of H_2O molecule is drawn as

Electronic information around the centre atom is given as
No. of Bond pair electrons = 2
No. of Lone pair electrons = 2

The repulsion of two lone pair electrons reduces the bond angle from 109.5° to 104.5°.
Hence the shape of H_2O molecule is Angular

CO_2 – Molecule

The Lewis structure of CO_2 molecule is drawn as

This shows that two sigma and two pi bond exists in the molecule. According to VSEPR theory pi bond are not involved in the repulsion and geometry because these are inactive electron pairs. Since only two active electron pairs are found around the carbon atom, its shape is Linear.

Short Questions

1. Define the following:

(i) Bond Energy **(ii) Bond length**

Ans)

Bond Energy: The energy involved for the breaking/formation of 1 mole of particular type of bonds in the molecule is known as bond energy.

Bond Length: The distance between the e nuclei of two bonded atoms in a molecule is known as bond length.

2. The Dipole moment of water is 1.85D but CO_2 has zero dipole moment why?

Ans) The dipole moment of a molecule depends on the distribution of charge within the molecule. Water (H2O) has a significant dipole moment (1.85 D) because its bent molecular structure leads to unequal charge distribution, with partial positive charges on hydrogen atoms and a partial negative charge on oxygen. In contrast, carbon dioxide (CO2) has a linear structure with symmetrical charge distribution, resulting in a net dipole moment of zero.

3. Differentiate between the following:

(i) VBT and MOT

(ii) Sigma bond and pi bond

(iii) Bonding M.O and Anti bonding M.O

Ans)

(i)

Valence Band Theory	Molecule Orbital Theory
Valence Bond theory tells that only some valence electrons are involved in the bond formation.	Molecular orbital theory tells that bond formation occurs due to the involvement of all the valence electrons of interacting atoms.
According to valence bond theory, both the concerned atomic orbitals possess their individual identity.	According to the molecular orbital theory, both the concerned atomic orbitals donot possess their individual identity.
VBT doesn't introduce any adequate idea about the bond order.	MOT gives adequate idea about the bond order by virtue of which, the bond can be identified as single, double or triple bond.
The paramagnetic behavior of molecules	The paramagnetic behavior of molecules

such as oxygen molecule (O_2) cannot be explained by valence bond theory.	are very well explained using molecular orbital theory.

(ii)

Sigma Bond	Pi Bond
It is formed by head to head overlapping of half filled atomic orbital.	It is formed by lateral/parallel overlapping of half filled atomic orbital.
Only one sigma bond can exist between the bonded atoms.	Maximum two pi bonds can form between the two atoms.
Orbital free rotation can be possible between the two atoms if only sigma bond is present.	Orbital free rotation is not possible between the two atoms if pi bond is present.
Electron cloud is denser at the plane of bond axis.	Electron cloud is denser at above and below the plane of bond axis.

(iii)

Characteristic	Bonding Molecular Orbitals (Bonding MOs)	Antibonding Molecular Orbitals (Antibonding MOs)
Formation	Formed by constructive overlap of atomic orbitals (in-phase).	Formed by destructive overlap of atomic orbitals (out-of-phase).
Energy Levels	Lower in energy than the constituent atomic orbitals.	Higher in energy than the constituent atomic orbitals.
Electron Density	Electrons are found between the nuclei of the bonded atoms.	Electrons are found away from the region between the nuclei.
Effect on Bonding	Contribute to bond stability and cohesion of the molecule.	Weaken or destabilize the bond between the atoms.

4. Explain the following with scientific reasons.

(i) Sigma bond is stronger than pi bond.

Ans) Sigma (σ) bonds are stronger than pi (π) bonds primarily because sigma bonds involve head-on overlap of orbitals along the bond axis, leading to more efficient electron sharing and a greater electron density between the bonding nuclei. In contrast, pi bonds involve sideways overlap of parallel p orbitals, which results in weaker electron density between the nuclei and, therefore, weaker bonding.

(ii) HF has greater ionic character than HCl.

Ans) Hydrogen fluoride (HF) exhibits greater ionic character than hydrogen chloride (HCl) due to the significantly higher electronegativity of fluorine compared to chlorine. This results in a more polar H-F bond with a larger difference in electron density. Additionally, the fluoride ion (F^-) formed in HF is smaller and more tightly bound than the chloride ion (Cl^-) in HCl, accentuating the ionic separation in HF. These factors collectively lead to HF displaying a higher degree of ionic character in its bonding compared to HCl.

(iii) Bond energy of molecules possessing multiple bonds is high.

Ans) Molecules with multiple bonds, such as double and triple bonds, have high bond energies due to several factors. These bonds involve greater electron density between atoms, extensive orbital overlap, shorter bond lengths, and higher bond dissociation energies. These characteristics collectively contribute to the stronger and more stable nature of multiple bonds, resulting in high bond energies.

5. Oil is insoluble in water but soluble in hexane explain why?

Ans) Oil is insoluble in water but soluble in hexane due to differences in polarity and intermolecular forces. Water is highly polar and forms strong hydrogen bonds, making it unsuitable for dissolving nonpolar oil. Hexane, on the other hand, is nonpolar like oil, facilitating favorable interactions between their similar nonpolar molecules and enabling oil to dissolve in it.

6. Which hybridization would you expect for the central atom in each of the following?

$BeCl_2$, BF_3, CH_4, C_2H_2

Ans)

Compounds	Elements
$BeCl_2$	sp
BF_3	sp^2
CH_4	sp^3
C_2H_2	sp

Descriptive Quesrions

1. (a) Write down the postulate of VSEPR theory

(b) Predict the shape of following molecules on the basis of VSEPR theory.

$AlCl_3$, CCl_4, PH_3, H_2S

Ans)

(a) Valence Shell Electron Pair Repulsion Theory (VSEPR): The main postulates of this theory are.

1. There may be two types of electron pairs surrounding the central atom.
   a. **Bond Pairs:** These are the result of the sharing of unpaired electrons of central atom with unpaired electrons of surrounding atoms. These are also called active set of electrons.
   b. **Lone Pairs:** These are the paired electrons of central atom which do not take part in sharing. They are also called non-bonding pairs. They are also considered to be active set of electrons.

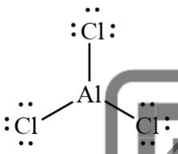
2. Being similarly charged (i.e. negative) the bond pairs as well as the lone pairs repel each other.
3. Due to repulsion, the electron pairs of central atom try to be as far apart as possible; hence they orient themselves in space in such a manner that force of repulsion between them is minimized.
4. The force of repulsion between lone pairs and bond pairs is not the same. The order of repulsion is as follow.

Lone pair-Lone pair repulsion > Lone pair-Bond pair repulsion > Bond pair-Bond pair repulsion.

5. In case of molecules with double and triple bonds, the electron pairs are not considered to be an active set of electrons, hence not included in the count of total electron pairs.
6. The shape of molecule depends upon total number of electron pairs (bonding and lone pairs).

The shape according to VSEPR theory is given below :

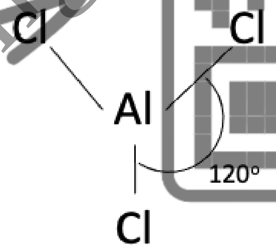
$AlCl_3$-molecule: We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.



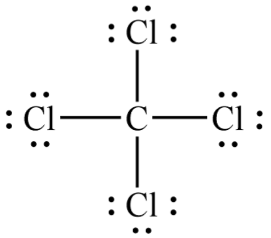
No. of Bond pair electrons = 3

No. of Lone pair electrons = 0

According to VSEPR, these three electron pairs repel to each other and directed towards the corner of triangle at an angle of 120° hence the geometry of molecule is trigonal planar.



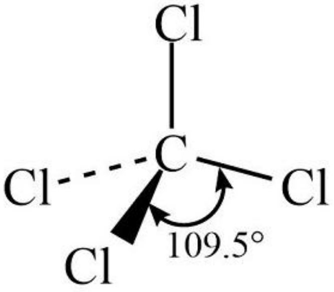
CCl_4-molecule: We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.



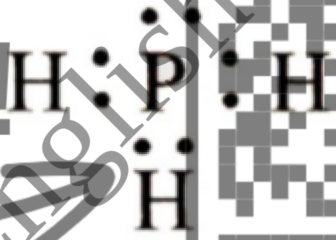
No. of Bond pair electrons = 4

No. of Lone pair electrons = 0

According to VSEPR, these three electron pairs repel to each other and directed towards the corner of tetrahedron at an angle of 109.5^o hence the geometry of molecule is tetrahedral.



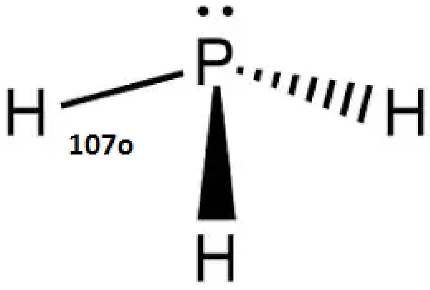
PH_3-molecule: We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.



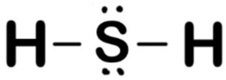
No. of Bond pair electrons = 3

No. of Lone pair electrons = 1

According to VSEPR, these three electron pairs repel to each other and directed towards the corner of pyramid at an angle of 107^o hence the geometry of molecule is trigonal pyramid.



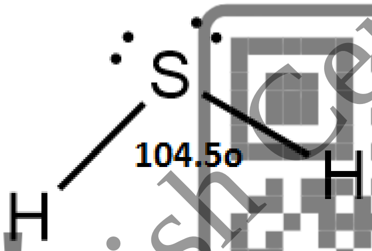
H_2S-molecule: We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.



No. of Bond pair electrons = 2

No. of Lone pair electrons = 2

According to VSEPR, the repulsion of two lone pair electrons reduces the bond angle from 109.5° to 104.5°. Hence the shape of H_2S molecule is Angular.



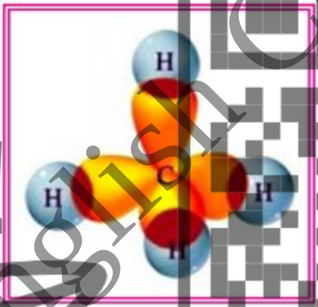
2. What do you mean by Hybridization? Explain sp^3 hybridization in CH_4 molecule and sp^2 hybridization in C_2H_4 molecule.

Ans) Hybridization: The mixing of different atomic orbital to produce the same number of equivalent orbital, having same shape and energy is known as hybridization". The orbitals so formed are called hybrid orbital.

sp^3 hybridization in CH_4 molecule: The electronic configuration of carbon is ($1s^2$, $2s^2$,$2px^1$, $2py^1$, $2px^0$) but it is assumed that one electron of 2s orbital get promoted to 2pz orbital to make it tetravalent.

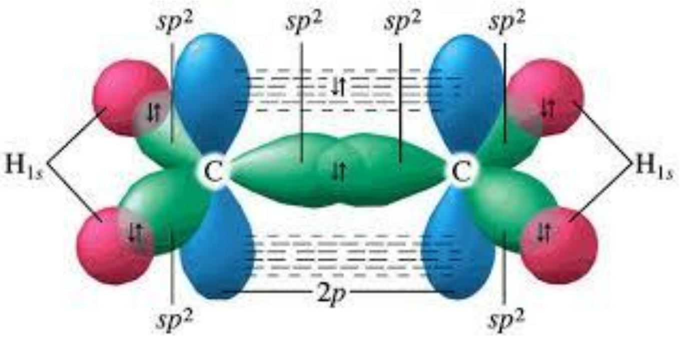
In methane, the four atomic orbital of carbon undergo a mixing process to produce four new orbital of equal energy and shape, each named as sp^3 hybrid orbital.

All four sp^3 hybrid orbital then directed towards the corner of a regular tetrahedron at an angle of 109.5°. Since each sp^3 hybrid orbital has one electron, it overlaps with Is orbital of hydrogen atom. Thus four C-H sigma bonds are formed.



Ethene molecule (C_2H_4): Ethene molecule consists of two central carbon, atoms. Each carbon possesses three sp^2 hybrid orbitals and one unhybridized pz orbital.

These three sp^2 hybrid orbital arrange themselves in triangular planar geometry at 120° angle. Two sp^2 orbitals of each carbon then overlap with s orbitals of two hydrogen atoms to form two C-H sigma bonds. The third sp^2 orbital of both carbon atoms overlap linearly with each other to form a C-C sigma bond. The unhybridized pz orbital of both carbon atoms which lie at right angle overlap side wise to form a pi bond.



3. What are the basic postulates of valence bond theory? Explain various type of overlapping lead to sigma and pi bond.

Ans) Valence Bond Theory: The main postulates of this theory are given below.

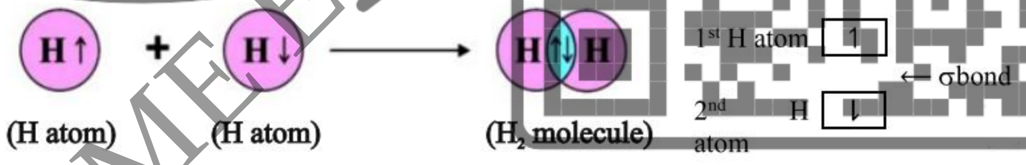
1. A covalent bond is formed due to the overlap of half filled orbital of combining atoms.
2. As a result of overlapping there is a maximum electron cloud somewhere between the two overlapped orbital.
3. The electrons present in both overlapped orbital should be in opposite spin.
4. The strength of bond is determined by the extent of overlap. The greater the overlap, the stronger is the bond.
5. Each atom involves in the overlapping keep its own atomic orbital but electron pair is shared up by both atoms which take part in the overlapping.

Types of overlapping:

s-s overlapping:

Definition: It is the overlap of half filled s orbital of two combining atoms.

Example: This type of overlapping exist in H_2 molecule. Hydrogen atom contains just one electron in Is-orbital. When the two hydrogen atoms come closer to each other, their half filled s-orbital overlap and form H-H sigma bond in which the electron cloud is rich along the axis between two nuclei.

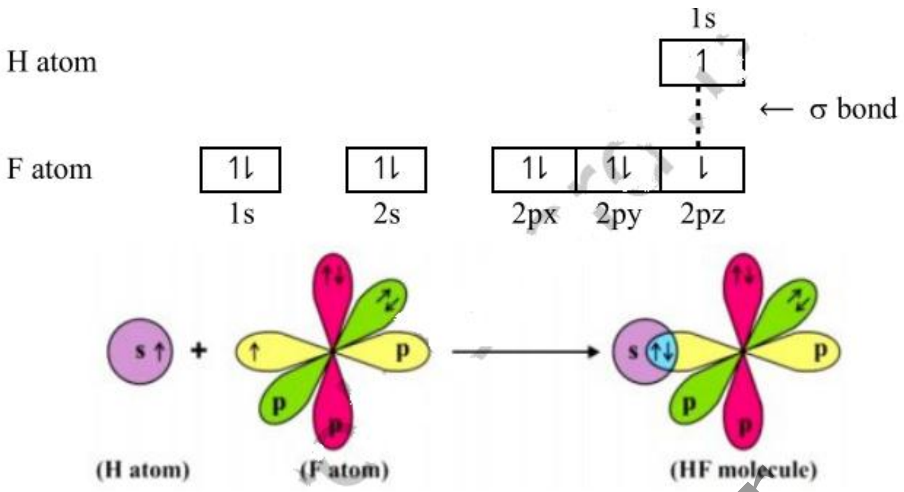


s- p overlapping:

Definition: It is the overlap of half filled s and half filled p orbital of two combining atoms.

Example: Example of molecule in which sigma bond is formed due to s-p overlapping are HF, HCI etc.

HF molecule is formed by overlap of half filled Is orbital of hydrogen atom and half filled 2pz orbital of fluorine.

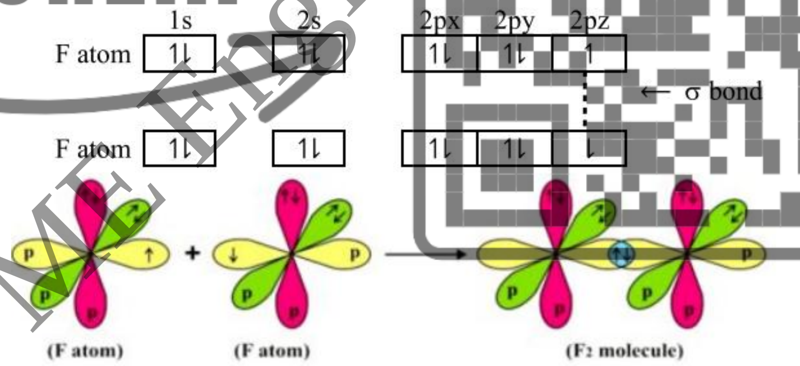


p-p overlapping:

Definition: It is the overlap of half filled p orbital of two combining atoms.

Example: The example of this type of overlapping is F_2 molecule.

The electronic configuration of fluorine is $1s^2\ s^2\ 2px^2\ 2py^2\ 2pz^1$, it means only pr orbital is occupied by single electron and available for overlap. VBT tells that, half filled pa orbital of both fluorine atoms undergo overlapping in which the electron pair is shared up between the two atoms.



4. Draw a molecular orbital diagram of O_2 molecule and

(i) Write down MO electronic configuration

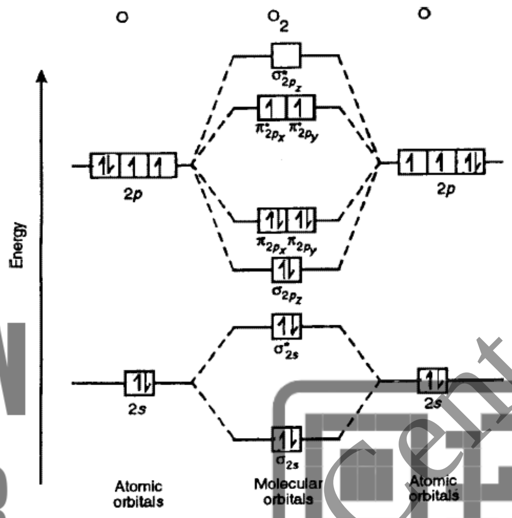
(ii) Determine bond order

(iii) Explain the paramagnetic behavior

Ans)

(i) MO electronic configuration of O_2 is $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^2$.

(ii) and (iii): As it can be seen from the MOT of O_2, The electrons in the highest occupied molecular orbital are unpaired therefore it is paramagnetic in nature. Also, the bond order can be calculated as $[N_b - N_a]/2 = [10-6]/2=2$. Therefore there is a double bond present as O=O.



Chapter 4: STATE OF MATTER I: GAS

Multiple Choice Question

1. Choose the correct answer:

(i) According to Graham's Law of diffusion, the ratio of diffusion of H_2 and O_2 are respectively:

(a) 1:2 (b) 2:1 (c) 1:4 (d) 4:1

(ii) Collection of gas over water is an example of:

(a) Graham's law (b) Dalton's law (c) Avogadro's law (d) Gay-Lussac law

(iii) The molar volume of oxygen gas is maximum at:

(a) 0°C and 1 atm (b) 0°C and 2 atm

(c) 25°C and 1 atm (d) 25°C and 2 atm

(iv) The diffusion rate of C_3H_8 and CO_2 are same because:

(a) Both are poly atomic gases (b) Both are denser than air

(c) Both have same molar mass (d) Both contains carbon atoms

(v) The volume of gas would be theoretically zero at:

(a) 0°C (b) 0 K (c) 273 K (d) 273°C

(vi) Real gas reaches the ideal behavior at:

(a) Low temperature and low pressure (b) High temperature and high pressure

(c) Low temperature and high pressure (d) High temperature and low pressure

(vii) Which one of the following statement is incorrect about the gas molecules?

(a) They have large spaces

(b) They possess kinetic energy

(c) Their collision is elastic

(d) Their molar mass depends upon temperature

(viii) If the Kelvin temperature of ideal gas is increase to double and pressure is reduce to one half, the volume of gas will:

(a) Remains same (b) Double (c) Reduced to half (d) Four time

(ix) The molar volume of oxygen gas is 22.4 dm³ at:

(a) 0°C and 1 atm (b) 25°C and 0.5 atm (c) 0 K and 1 atm (d) 25 K and 0.5 atm

(x) Under similar condition CH_4 gas diffuses......... times faster than SO_2 gas:

(a) 1.5 time (b) 2 times (c) 4 times (d) 16 times

KEY:

i. d	ii. b	iii. c	iv. c	v. b
vi. d	vii. d	viii. d	ix. a	x. c

Example 4.1

The pressure of gas filled in automobile tire is generally measured in psi convert 32.8 psi into (i) atmosphere (ii) Kpa (iii) torr

Solution:

(i) Psi to atmosphere

Since 14.7 psi = 1 atm

$32.8 \text{ psi} = \frac{32.8}{14.7} = 2.23 \text{ atm}$

(ii) Psi to Kilo Pascal

Since 14.7 psi = 101.325 Kpa

$32.8 = \frac{101.325}{14.7} \times 32.8 = 226.085 \text{ KPa}$

(iii) Psi to torr

Since 14.7 psi = 760 torr

$32.8 \text{ psi} = \frac{760}{14.7} \times 32.8 = 1695.8 \text{ torr}$

Example 4.2

A cylinder contains 2.2 moles of oxygen gas at S.T.P. When more oxygen gas is pumped into the cylinder, the volume of a gas is changed from 2.0 dm^3 to 3.4 dm^3. Calculate how many moles of the oxygen gas are added to the cylinder?

Solution:

$V_1 = 2.0 \text{ dm}^3$

$n_1 = 2.2 \text{ moles}$

$V_2 = 3.4 \text{ dm}^3$

$n_2 = ?$

Applying Avogadro's Law

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Substituting the values

$$\frac{2.0}{2.2} = \frac{3.4}{n_2}$$

$$n_2 = \frac{3.4 \times 2.2}{2.0}$$

$n_2 = 3.74 \text{ moles}$

$\Delta n = n_2 - n_1$

$\Delta n = 3.74 - 2.2 = 1.54 \text{ moles}$

Example 4.3

Laughing gas (N_2O) at 30°C and 820 torr pressure occupies a volume of 10.32 dm^3. Calculate the volume that it will occupy at standard temperature and pressure.

Solution:

$T_1 = 30°C = 30 + 273 = 303k$

$P_1 = 820$ torr

$V_1 = 10.32\ dm^3$

$V_2 = ?$

$T_2 = 273k$

$P_2 = 760$ torr

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{820 \times 10.32 \times 273}{303 \times 760}$$

$V_2 = 10.03\ dm^3$

Example 4.4

Calculate the density of oxygen gas at 45 °C when the gas is confined in cylinder at 1.54 atmospheric pressure.

Solution:

$d = ?$

$T = 45°C = 45 + 273 = 318\ K$

$P = 1.54$ atm

$R = 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1}$

$M_{O2} = 32\ g\ mol^{-1}$

The formula of density derived from general gas equation is given as

$$d = \frac{PM}{RT}$$

By substituting the values, we get

$$d = \frac{1.54 \times 32}{0.0821 \times 318}$$

$d = 1.889\ g/dm^3$

Example 4.5

One mole of ammonia gas is kept in a cylinder of $5.5 dm^3$ at 27°C. Assuming ammonia gas as a real gas determine its pressure. The ven der Waal constant for ammonia are a = 4.17 atm dm^6 mol^{-2} and b = 0.0371 dm^3 mol^{-1}.

Solution:

n = 1 mole

T = 27°C = 27 + 273 = 300K

V = 5.5 dm^3

R = 0.0821 atm dm^3 mol^{-1} K^{-1})

P = ?

According to van der waal equation.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{4.17 \times 1}{(5.5)^2}\right)(5.5\text{-}0.0371) = (1)(0.082 \times 300)$$

$$(P + 0.138)(5.462) = 24.6$$

$$P = 4.365 \text{ atm}$$

Example 4.6

Two moles of oxygen gas is kept in a vessel of $15.5 dm^3$ at a temperature of 37°C. Calculate the pressure exerted by the gas if

(a) gas behave as ideal (b) gas behave is non ideal

The ven der waal constant of O_2 gas are given as

a = 1.36dm^6 atm mol^{-2} and b = 0.0318 dm^3 mol^{-1}.

Solution:

n = 2 moles

T = 37 °C = 37+273 = 310 K

V = 15.5 dm^3

R = 0.0821 atm dm^3 mol^{-1} K^{-1})

P = ?

i) General gas equation is used if gas behave ideally,

PV=nRT

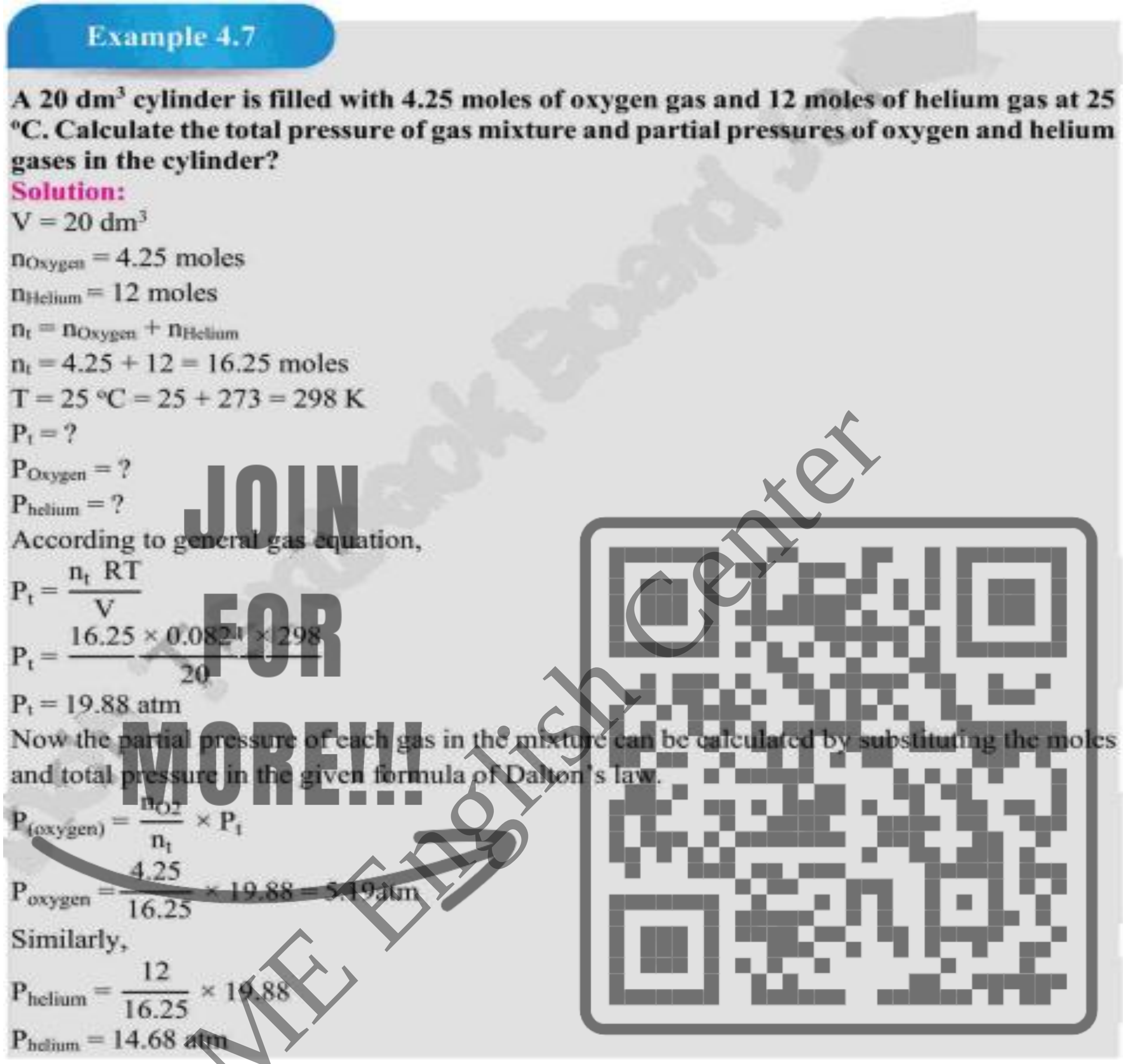
$$P = \frac{2 \times 0.0821 \times 310}{15.5} = 3.28 \text{ atm}$$

ii) van der Waal equation is used if it behaves as non ideal gas

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{1.36 \times 4}{(15.5)^2}\right)(15.5\text{-}2 \times 0.0318) = 2 \times 0.082 \times 310$$

$$P = 3.27 \text{ atm}$$



Example 4.7

A 20 dm^3 cylinder is filled with 4.25 moles of oxygen gas and 12 moles of helium gas at 25 °C. Calculate the total pressure of gas mixture and partial pressures of oxygen and helium gases in the cylinder?

Solution:

$V = 20\ dm^3$

$n_{Oxygen} = 4.25$ moles

$n_{Helium} = 12$ moles

$n_t = n_{Oxygen} + n_{Helium}$

$n_t = 4.25 + 12 = 16.25$ moles

$T = 25\ °C = 25 + 273 = 298\ K$

$P_t = ?$

$P_{Oxygen} = ?$

$P_{helium} = ?$

According to general gas equation,

$$P_t = \frac{n_t\ RT}{V}$$

$$P_t = \frac{16.25 \times 0.0821 \times 298}{20}$$

$P_t = 19.88$ atm

Now the partial pressure of each gas in the mixture can be calculated by substituting the moles and total pressure in the given formula of Dalton's law.

$$P_{(oxygen)} = \frac{n_{O2}}{n_t} \times P_t$$

$$P_{oxygen} = \frac{4.25}{16.25} \times 19.88 = 5.19 atm$$

Similarly,

$$P_{helium} = \frac{12}{16.25} \times 19.88$$

$P_{helium} = 14.68$ atm

Example 4.8

Oxygen gas is produced by heating potassium nitrate

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

The gas is collected over water. If 225cm³ of gas is collected at 25°C and 785mm Hg total pressure, what is the mass of O_2 gas collected? (Pressure of vapours at 25°C is 23.8 mm Hg)

Solution:

According to Dalton's law, the total pressure of mixture is equal to the sum of partial pressure of O_2 and vapours thus

$P_t = P_{(O2)} + P(\text{vapours})$

Hence

$P_{(O2)} = 785 - 23.8 = 761.2$ mmHg

Convert the units of pressure from mm Hg to atm & unit of volume from cm³ to dm³

$P = \frac{761.2}{760} = 1.001$ atm;

$V = 225cm^3 = \frac{225}{1000} = 0.225dm^3$

$T = 25°C = 25 + 273 = 298K$

We can use general gas equation to determine the number of moles of oxygen gas

$PV = nRT$

$n = \frac{1.001 \times 0.225}{0.082 \times 298} = 9.2 \times 10^{-3}$ moles

Now, mass of $O_2 = 9.2 \times 10^{-3} \times 32 = 0.294g$

Example 4.9

Compare the rates of diffusion of helium (H_e) and methane (CH_4) gases.

Solution:

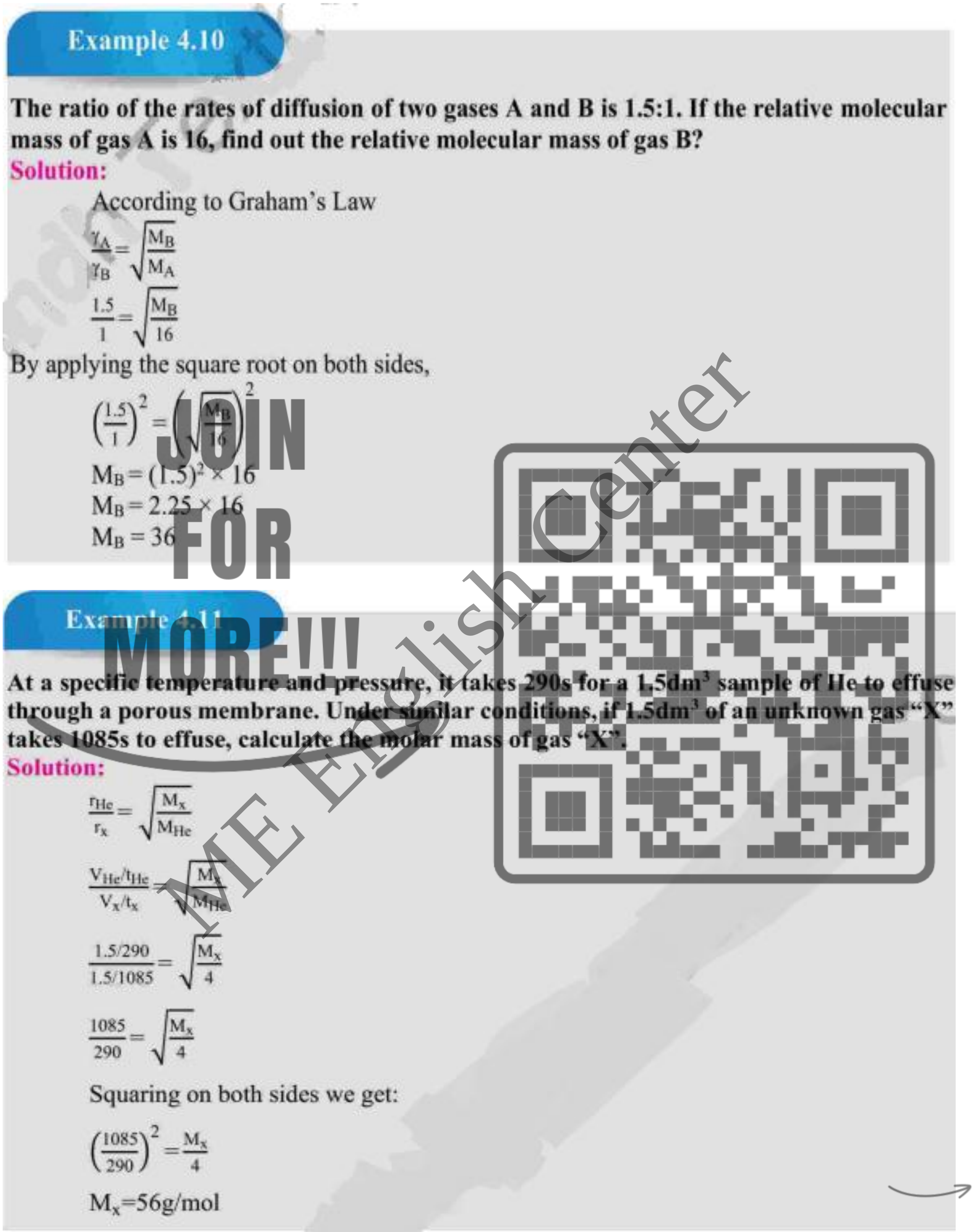
Mass of He = 4 a.m.u

Molecular mass of CH_4 = 12 + 4 = 16 a.m.u

$$\frac{rHe}{rCH_4} = \sqrt{\frac{MCH_4}{MHe}}$$

$$\frac{rHe}{rCH_4} = \sqrt{\frac{16}{4}} = \frac{4}{2} = \frac{2}{1} \text{ Ans}$$

Thus helium diffuses two times as fast as CH_4.



Example 4.10

The ratio of the rates of diffusion of two gases A and B is 1.5:1. If the relative molecular mass of gas A is 16, find out the relative molecular mass of gas B?

Solution:

According to Graham's Law

$$\frac{\gamma_A}{\gamma_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{1.5}{1} = \sqrt{\frac{M_B}{16}}$$

By applying the square root on both sides,

$$\left(\frac{1.5}{1}\right)^2 = \left(\sqrt{\frac{M_B}{16}}\right)^2$$

$$M_B = (1.5)^2 \times 16$$

$$M_B = 2.25 \times 16$$

$$M_B = 36$$

Example 4.11

At a specific temperature and pressure, it takes 290s for a 1.5dm^3 sample of He to effuse through a porous membrane. Under similar conditions, if 1.5dm^3 of an unknown gas "X" takes 1085s to effuse, calculate the molar mass of gas "X".

Solution:

$$\frac{r_{He}}{r_x} = \sqrt{\frac{M_x}{M_{He}}}$$

$$\frac{V_{He}/t_{He}}{V_x/t_x} = \sqrt{\frac{M_x}{M_{He}}}$$

$$\frac{1.5/290}{1.5/1085} = \sqrt{\frac{M_x}{4}}$$

$$\frac{1085}{290} = \sqrt{\frac{M_x}{4}}$$

Squaring on both sides we get:

$$\left(\frac{1085}{290}\right)^2 = \frac{M_x}{4}$$

$$M_x = 56\text{g/mol}$$

Short Questions

1. State the following gas laws.

(i) Avogadro's law **(ii) Charles law**

Ans)

(i) Avogadro's law: The volume of the given mass of a gas is inversely proportional to its pressure at constant temperature.

(ii) Charles law: The volume of given mass of a gas is directly proportional to the absolute temperature at a given pressure.

2. State main postulates of kinetic molecular theory of gas.

Ans)

Postulates of Kinetic Molecular Theory of gas: The basic postulates of kinetic theory of gases are as follows.

(i) Gases consist of a large number of tiny particles called molecules. Molecules may be monoatomic (He, Ne, Ar), diatomic (O_2, N_2) or poly atomic (CH_4, C_4H_{10}).

(ii) Gas molecules are far away from each other and occupy negligible volume as compared to the total volume of the container.

(iii) Gas molecules are in continuous random motion, traveling in a straight line until they collide with each other or with the walls of the container. The average distance covered by the gas between successive collisions is known as mean free path.

(iv) Gas particles undergo elastic collisions (a collision in which no loss or gain of energy takes place).

(v) Gas exerts pressure when molecules collide with the walls of container.

(vi) There is no force of attraction or repulsion found among ideal gas molecules, each molecule acts as quite independently.

(vii) The average kinetic energy of gas molecules depends upon absolute temperature.Thus when absolute temperature increases kinetic energy of the molecules increases.

$$KE \propto \text{Absolute temperature}$$

3. Explain the following:

(i) Pressure and its various units **(ii) Absolute zero**

Ans)

(i) Pressure:

Definition: The magnitude of force that is applied on the surface of an object per unit area.

Mathematical form:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

S.I unit: Its S.I unit is N/m^2 which is known as Pascal (Pa).

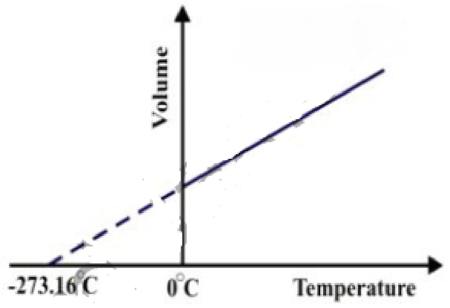
Pascal (Pa): One Newton force that is distributed at an area of one square meter.

Alternative units of pressure and their inter relation: Certain alternative units of pressure and their inter relation are given as

101325 Pa = 1 atm = 760 mm Hg = 14.7 psi

Atmospheric pressure: The atmospheric pressure is a thermodynamic property which is created by the mass of air molecules on the surface of earth.

(ii) **Absolute zero:** According to Charles, at 0K (-273.15 °C) the volume of a gas should be zero. Actually no real gas can achieve this lowest possible temperature and before-273.15°C all gases are condensed in to liquids. Zero Kelvin is also known as Absolute zero. The concept of absolute zero cannot be applied to real gases.



Graphical representation of the absolute zero.

4. What is liquid air? Mention its three uses.

Ans)

Liquid air: Ordinary air on compression and cooling to extremely low temperature becomes liquefies and known as liquid air.

Uses of liquid gases: Some important uses of liquefied gases are given below.

1. Liquefied natural gas (L.N.G) is used as a fuel.
2. Liquefied petroleum gas (L.P.G) is a mixture of butane and other hydrocarbons, used as a fuel for portable heaters, gas cooktops and ovens. It is also used as fuel for engines.
3. Ammonia and liquid sulphur dioxide are used as refrigerants.

5. What is plasma? Give its significance in daily life.

Ans) Plasma (Forth state of matter): The mixture of positive ions, electrons and un- ionized molecules and atoms is known as plasma.

Significance in daily life:

1. It is used in television and computer chips.
2. Plasma is used in rocket propulsion, cleaning the environment, destroying biological hazards and healing wounds.

Descriptive Questions

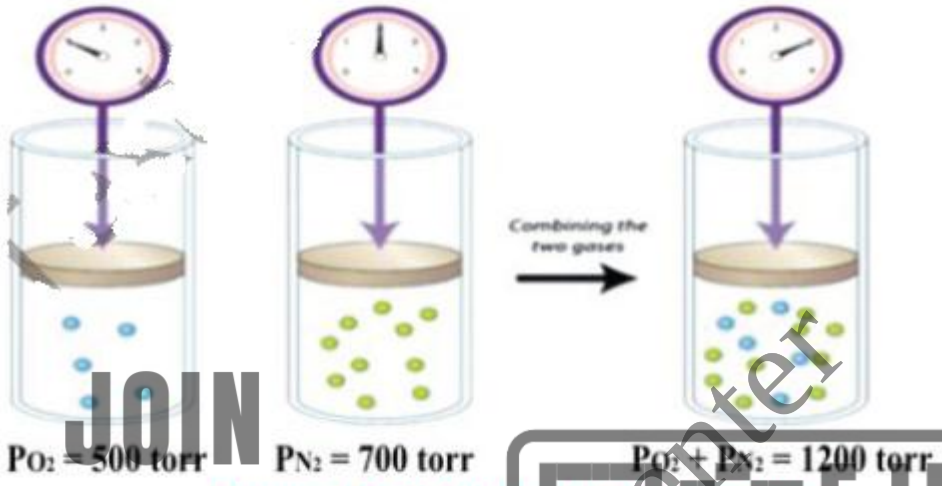
1. State and explain Dalton's law of partial pressure. Give practical applications of Dalton's law.

Ans)

Dalton's law of partial pressure:

Statement: The total pressure exerted by a mixture of non reacting gases in a closed vessel (fixed volume) is always equal to the sum of their individual pressures at a constant temperature.

Example: Suppose we have three empty cylinders of equal capacity (1 dm^3), O_2 and N_2 gases are filled separately in first two cylinders at constant temperature. Let the pressure exerted by the O_2 gas and N_2 gas are 500 torr and 700 torr respectively. If now these gases are transferred into third empty cylinder under the condition of same temperature; the pressure exerted by the mixture gases is found to be 1200 torr which is exactly equal to the sum of partial pressure of O_2 and N_2.



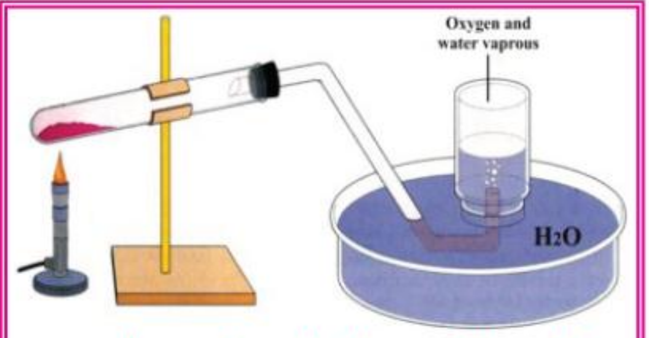
Pressure of individual gases and of their mixture

Applications of Daltons Law of partial pressure:

(i) Pressure of gases collected over water: When a gas is collected over water by downward displacement of water in a gas jar, the pressure of dry gas can be calculated by Daltons Law. When gas passes through water, it becomes moist and the total pressure will be equal to the sum of partial pressure of dry gas and water vapors (aqueous tension).

$$P_{total} = P_{dry\ gas} + P_{water\ vapors}$$

$$P_{dry\ gas} = P_{total} - P_{water\ vapors}$$



Pressure of gas collected over water is equal to the sum of pressure of dry gas and vapours

(ii) Maintenance of oxygen pressure at high altitudes: The pressure of air on high altitudes is lower than sea level due to decrease in number of molecules of gases. Normally, respiration depends upon the difference between the partial pressure of oxygen in the air (159 torr) and in the lungs (116 torr). At higher altitudes, due to low partial pressure of oxygen causes the problem in the process of respiration.

(iii) Maintenance of oxygen pressure for deep sea divers: Opposite to altitude, as distance increases downward in the sea, partial pressure of oxygen increases. At the depth of 40 meters, pressure increases to five times. This increased pressure also causes problem in respiration. Therefore, deep sea divers use the SCUBA (Self Contained Underwater Breathing Apparatus), breathing tank for respiration. Scuba contains 96% helium gas and 4% oxygen gas.

2. Derive general gas equation. Also deduce the value of R in atm dm^3/mol.K and J/mol.K.

Ans)

Derivation of an ideal gas equation:

According to Boyle's Law $V \propto \frac{1}{P}$ (At constant temperature)

According to Charles's Law $V \propto T$ (At constant pressure)

According to Avogadro's Law $V \propto n$ (At constant temperature and pressure)

$$V \propto \frac{nT}{P}$$

$$V = \frac{RnT}{P}$$

And $PV = nRT$

Where, R is general gas constant.

For one mole of a gas this equation can be written as:

$$PV=RT$$

$$R=\frac{PV}{T}$$

If we change the pressure from P_1 to P_2 and temperature from T_1 to T_2, then the above equation can be written as:

$R=\frac{P_1V_1}{T_1}$ and $R=\frac{P_2V_2}{T_2}$

Therefore,

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}=\frac{P_nV_n}{T_n}$$

(a) Value of R when pressure is in atmosphere and volume in dm^3:

We know that one mole of an ideal gas at S.T.P (one atmosphere pressure and 273 K) occupies 22.4 dm^3.

$$R=\frac{PV}{nT}$$

$$R=\frac{1\ \text{atmosphere}\times 22.4\ dm^3}{1\ \text{mole}\times 273k}$$

$R=0.0821$ atm dm^3 $mole^{-1}$ K^{-1}

(b) Value of R when pressure is in N/m^2 and volume in m^3 (S.I unit):

According to the S.I system, pressure is measured in N/m^2 and volume in m^3.

since 1 atm = $101325 N/m^2$

And 1 dm^3 = 0.0224 m^3

$$R=\frac{PV}{nT}$$

$$R=\frac{101300\times 0.0224}{1\ \text{mol}\times 273}$$

$R=8.31 Nm\ mol^{-1} k^{-1}$

$R=8.31\ J\ mol^{-1}\ k^{-1}$ (Because 1 Nm = 1J)

3. How an ideal gas is differentiated from real gas? What are the causes of deviation of real gas from ideal behavior? Explain this deviation at low temperature and high pressure.

Ans)

Ideal Gases:

- Hypothetical gases with negligible particle size and no intermolecular forces.
- Follow the ideal gas law (PV = nRT) exactly.

- Applicable at low pressures and high temperatures.

Real Gases:

- Composed of molecules with finite size and intermolecular forces (Van der Waals forces).
- Deviate from ideal gas law at high pressures and low temperatures.
- Have a compressibility factor (Z) that can vary from 1, indicating attractive or repulsive forces.
- Require specialized equations of state at extreme conditions.

Causes of deviation of real gases from ideal behavior:

To analyze why real gases deviate from ideal behavior, we should know the basics on which the ideal gas equation was formulated. The ideal gas equation was obtained from certain assumptions of kinetic molecular theory; two main assumptions are given below.

1. The actual volume of the gas molecules is negligibly small as compared to the total space of the container.
   This assumption remains valid at low pressure where the volume of gas is much larger due to large intermolecular spaces but at high pressure gas is in the compressed state and the volume of gas molecules becomes significant as compared to the volume of gas enclosed in the container.
2. Gas molecules have neither attractive nor repulsive forces.
   This assumption is valid at low pressure and high temperature at which molecules tend to be far apart, because these forces diminish rapidly as the distance between molecules increases. But at high pressure and low temperature intermolecular forces becomes significant because molecules tend to be close together.

Deviation at low temperature and high pressure:

1. **Molecular Volume:** In the ideal gas model, gas molecules are considered to have negligible volume. This means that they are treated as point particles with no physical size. However, in the real world, gas molecules do have a finite volume. At high pressures, as gas molecules are forced closer together, the volume they occupy becomes significant compared to the total volume of the gas. This reduces the available space for the gas particles to move, leading to a decrease in the volume available for the gas itself.

2. **Intermolecular Forces:** Real gas molecules interact with each other through intermolecular forces, such as Van der Waals forces. At low temperatures, the kinetic energy of gas molecules is relatively low, making them more susceptible to these intermolecular forces.
3. **Deviation from Ideal Gas Law:** The ideal gas law, represented as PV = nRT, assumes that gas molecules have zero volume and do not interact with each other. Under low-temperature, high-pressure conditions, real gas molecules deviate from this ideal behavior. These deviations can result in lower observed pressures (compared to what the ideal gas law predicts) because attractive forces between molecules tend to reduce the pressure exerted on the container walls, and the finite volume of gas molecules reduces the available volume for the gas.

4. What is meant by diffusion and effusion? Explain Graham's law of diffusion.

Ans)

Effusion:

Definition: The movement of gas molecules through tiny hole into the region of low pressure is termed as Effusion.

Example: Slow escaping of air from a tyre pinhole is an example of effusion.

Diffusion:

Definition: The process by which particles of one substance spread out through the particles of another substance.

Example: The spreading of fragrance of a rose flower or a perfume is because of diffusion.

Graham's law of diffusion:

Statement: At constant temperature and pressure, the rate of effusion or diffusion of a gas is inversely proportional to the square root of its density or molar mass.

Derivation: If 'r' is rate of diffusion and 'd' is density of a gas then according to Graham's law:

$$r \propto \frac{1}{\sqrt{d}} \text{ (At constant temperature and pressure)}$$

$r = \frac{k}{\sqrt{d}}$ Where, k is constant for proportionality.

If we consider two gases 1 and 2, having rates of diffusion r_1 and r_2 and densities d; and d respectively then:

$$r_1 = \frac{k}{\sqrt{d_1}} \text{ ....(i)}$$

$$r_2 = \frac{k}{\sqrt{d_2}} \text{ ....(ii)}$$

Now divide equation (i) with equation (ii), we get:

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \text{ ....(iii)}$$

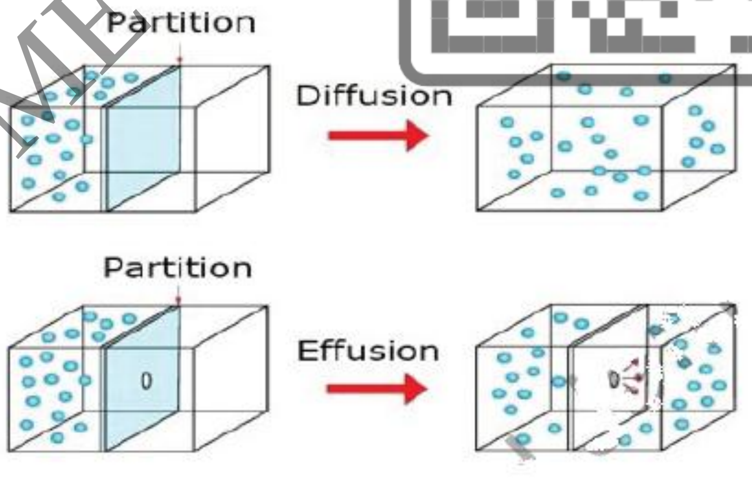
The density of a given gas is directly proportional to its molecular mass, therefore,

$$d_1 = \frac{M_1}{V} \text{ and } d_2 = \frac{M_2}{V}$$

We can write the equation (iii) as:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \text{.........(iv)}$$

Where, M_1 and M_2 are the molar masses of gases.



Diffusion and Effusion of gases

Numerical Questions

1. Gorakh hill station is the coldest area of Sindh province and has 83 kPa barometer pressure. What will be the pressure of this area in psi and atm units?

Data:

Pressure in kPa = 83 kPa

Pressure in psi = ?

Pressure in atm = ?

Solution:

Pressure in psi = 83 x 0.145 = 12.035 psi

Pressure in atm = 83 x 0.00987 = 0.819 atm

2. Calculate the volume occupied by 8g of methane gas at 40°C and 842 torr pressure.

Data:

V = ?

m = 8g

T = 40°C + 273 = 313 K

P = 842 torr = 842 / 760 = 1.108 atm

Solution:

$n = \frac{m}{M}$

$n = \frac{8}{16}$ = 0.5 moles

R = 0.0821 atm dm^3 $mole^{-1}$ K^{-1}

PV = nRT

(1.108) V = (0.5) (0.0821) (313)

V = 11.596 dm^3

3. At 35°C, oxygen gas in a cylinder has 456 cm³ volume and 0.85 atm pressure: Calculate the pressure when this oxygen gas is transferred to 10 dm^3 cylinder and cooled to 20°C.

Data:

T_1 = 35°C = 35 + 273 = 308 K

V_1 = 456 cm³ = 456/1000 = 0.456 dm^3

P_1 = 0.85 atm

P_2 = ?

V_2 = 10 dm^3

T_2 = 20°C = 20 + 273 = 293

Solution:

$$\frac{P_1\,V_1}{T_1} = \frac{P_2\,V_2}{T_2}$$

$$\frac{(0.85)(0.456)}{308} = \frac{P_2\,(10)}{293}$$

P_2 = 0.037 atm

4. Compare the rates of diffusion of the following pairs of gases:

(1) H_2 and He **(2) He and SO_2** **(3) SF_6 and SO_2**

Data:

(1) $\sqrt{\frac{r_{H_2}}{r_{He}}}$ = ?

(2) $\sqrt{\frac{r_{He}}{r_{SO_2}}}$ = ?

(3) $\sqrt{\frac{r_{SF_6}}{r_{SO_2}}}$ = ?

Solution:

$$\boldsymbol{\sqrt{\frac{r_{H_2}}{r_{He}}} = \sqrt{\frac{4}{2}} = \frac{1.41}{1}}$$

$$\sqrt{\frac{r_{He}}{r_{SO_2}}} = \sqrt{\frac{64}{4}} = \frac{4}{1}$$

$$\sqrt{\frac{r_{SO_2}}{r_{SF_6}}} = \sqrt{\frac{146}{64}} = \frac{1.51}{1}$$

5. Four containers of equal volume are filled as follows:

(i) 2.0g of H_2 at 0°C (ii) 1.0 g of H_2 at 273 ^oC

(iii) 24g of O_2 at 0°C (iv) 16 g of CH_4 at 273 ^oC

(a) Which container is at the greatest pressure?

(b) Which container is at the lowest pressure?

Data:

(i)

$m_{H2} = 2.0g$

$T_{H2} = 0 + 273 = 273$ K

(ii)

$m_{H2} = 1.0g$

$T_{H2} = 273 + 273 = 546$ K

(iii)

$m_{O2} = 24$ g

$T_{O2} = 0 + 273 = 273$ K

(iv)

$m_{CH4} = 16$ g

$T_{CH4} = 273 + 273 = 546$ K

(a) Which container is at the greatest pressure = ?

(b) Which container is at the lowest pressure = ?

Solution:

We are taking volume equals to 1 dm^3

(i)

$n_{H2} = \frac{m_{H2}}{M_{H2}} = \frac{1}{2} = 0.5$ moles

$P_{H2}\ V_{H2} = n_{H2}\ R_{H2}\ T_{H2}$

$(P_{H2})\ (1) = (0.5)\ (0.0821)\ (546)$

$P_{H2} = 22.4133$ atm

(ii)

$n_{H2} = \frac{m_{H2}}{M_{H2}} = \frac{1}{2} = 0.5$ moles

$P_{H2}\ V_{H2} = n_{H2}\ R_{H2}\ T_{H2}$

$(P_{H2})\ (1) = (0.5)\ (0.0821)\ (546)$

$P_{H2} = 22.4133$ atm

(iii)

$N_{O2} = \frac{m_{O2}}{M_{O2}} = \frac{24}{32} = 0.75$ moles

$P_{O2}\ V_{O2} = n_{O2}\ R_{O2}\ T_{O2}$

$(P_{O2})\ (1) = (0.75)\ (0.0821)\ (273)$

$P_{O2} = 16.8099$ atm

(iv)

$N_{O2} = \frac{m_{CH4}}{M_{CH4}} = \frac{16}{16} = 1$ moles

$P_{CH4}\ V_{CH4} = n_{CH4}\ R_{CH4}\ T_{CH4}$

$(P_{CH4})\ (1) = (1)\ (0.0821)\ (546)$

$P_{CH4} = 44.8266$ atm

(a) iv **(b) iii**

6. A 500 cm³ vessel contains H_2 gas at 400 torr pressure and another 1 dm³ vessel contains O_2 gas at 600 torr pressure. If under the similar condition of temperature these gases are transferred to 2 dm^3 empty vessel, calculate the pressure of the mixture of gases in new vessel.

Data:

V_{H2} = 500 cm³ = 500/1000 = 0.5 dm^3

P_{H2} = 400 torr

V_{O2} = 1 dm³

P_{O2} = 600 torr

V_T = 2 dm^3

P_T = ?

Solution:

$P_{H2}\ V_{H2} + P_{O2}\ V_{O2} = P_T\ V_T$

$(400)\ (0.5) + (600)\ (1) = P_T\ (2)$

P_T = 400 torr

7. If 16 cm^3 of hydrogen effuses in 30 sec, from a porous material, what volume of SO_2 will effuse in the same time (30 sec.) under similar conditions?

Data:

V_{H2} = 16 cm^3

t_{H2} = 30 sec

V_{SO2} = ?

t_{SO2} = 30 sec

Solution:

$$\frac{r_{SO2}}{r_{H2}} = \sqrt{\frac{M_{H2}}{M_{SO2}}}$$

$$\frac{V_{SO2}}{t_{SO2}} \div \frac{V_{H2}}{t_{H2}} = \sqrt{\frac{M_{H2}}{M_{SO2}}}$$

$$\frac{V_{SO_2}}{t_{SO_2}} \times \frac{t_{H_2}}{V_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{SO_2}}}$$

$$\frac{V_{SO_2}}{30} \times \frac{30}{16} = \sqrt{\frac{2}{64}}$$

$V_{SO_2} = 2.828\ cm^3$

8. 40 dm^3 of hydrogen gas was collected over water at 831 torr pressure at 23°C. What would be the volume of dry hydrogen gas at standard conditions? The vapour pressure of water at 23°C is 21 mm of Hg.

Data:

$V = 40\ dm^3$

$P = 831 - 21 = 810$ torr

$T = 23°C = 23 + 273 = 300$ K

$V_1 = ?$

Solution:

$$\frac{PV}{T} = \frac{P_1V_1}{T_1}$$

$$\frac{(810)(40)}{300} = \frac{(760)(V_1)}{273}$$

$V_1 = 38.795\ dm^3$

Chapter 5: STATE OF MATTER II: LIQUIDS

Multiple Choice Questions

1. Choose the correct answer:

(i) The boiling point of water (H_2O) is 100°C where as that of hydrogen sulphide (H_2S) is 42°C, This can be attributed to:

(a) Smaller bond angle of H_2S than H_2O

(b) Smaller radii of oxygen than sulphur

(c) High IP of oxygen than sulphur

(d) Tendency of water to form hydrogen bond

(ii) Liquids can form convex meniscus in a narrow glass tube when:

(a) Cohesive forces are stronger than adhesive forces

(b) Adhesive forces are stronger than cohesive forces

(c) Cohesive and adhesive forces are equal in strength

(d) None of these

(iii) Which of the following statement is incorrect?

(a) Viscosity is the resistance against flow of liquid

(b) Liquid possess definite volume

(c) One feels sense of cooling after bath due to condensation

(d) Sublimation is endothermic process.

(iv) Which of the following possesses weakest London dispersion forces:

(a) Cl_2 (b) F_2 (c) Br_2 (d) I_2

(v) Hydrogen bond is not found in:

(a) H_2O (b) CH_4 (c) NH_3 (d) HF

(vi) The boiling points of different liquids may be different at the same external pressure due to:

(a) Amounts of liquids (b) Intermolecular forces (c) Surface area (d) Viscosities

(vii) Which statement is incorrect about evaporation?

(a) It is an exothermic process

(b) It is a reverse process of condensation

(c) It occurs at all temperature and pressure

(d) It causes cooling effect

(viii) Which of the following liquids show maximum surface tension?

(a) Water (b) Mercury (c) Ethyl alcohol (d) Gasoline

(ix) A non-polar molecule with bigger size will experience:

(a) London forces (b) dipole-dipole interaction (c) Hydrogen bonding (d) All of these

(x) Cooking time is reduced in a pressure cooker because:

(a) Boiling point of water increases (b) Boiling point of water decreases

(c) Vapor pressure of liquid is reduced (d) Heat is uniformly distributed

KEY:

i. d	ii. a	iii. c	iv. b	v. d
vi. b	vii. a	viii. b	ix. a	x. a

Short Questions

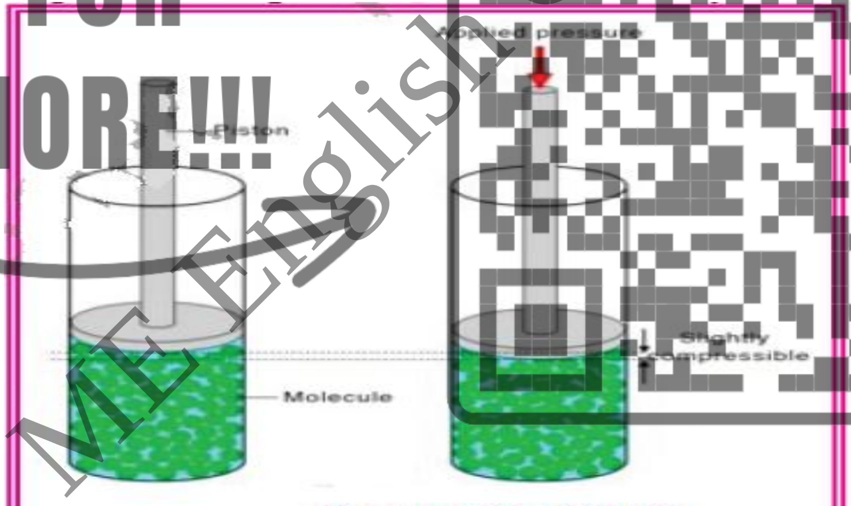
1. Explain the following in terms of kinetic molecular interpretation of liquids:

(a) Diffusion (b) Compression (c) Expansion (d) Molecular motion

Ans)

(a) Diffusion: Two miscible liquids diffuse into each other, however the process of diffusion in liquids is slower than gases due to small intermolecular gaps which cause difficulties in molecular movement. For example a drop of ink spreads in a glass full of water slowly.

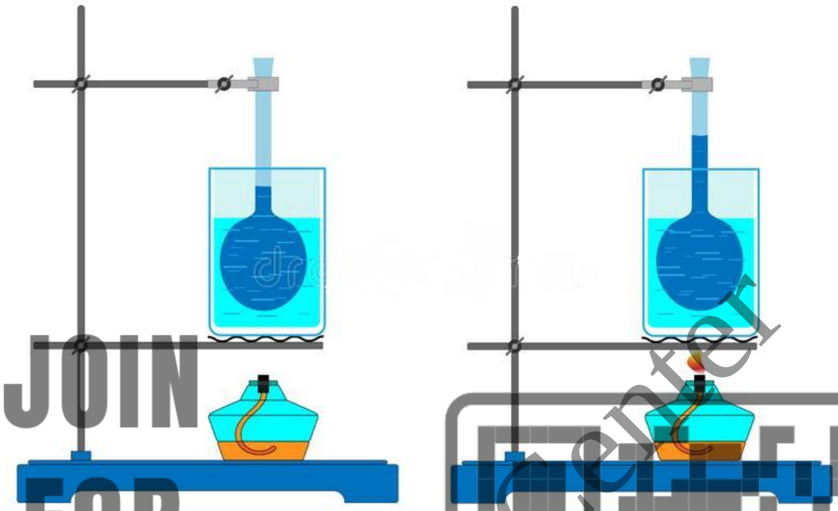
(b) Compression: Liquids are very less compressible as compared to the gases. In term of kinetic molecular theory liquid molecules are in constant random motion in small intermolecular spaces hence if we put a pressure on liquid its volume does not appreciably change. An example of compression of liquid is hydraulic brakes system in automobile.



Compression of liquid

(c) Expansion: Liquids expand on heating. However they do not show appreciable increase in their volumes by heating like gases do. Expansion is due to high kinetic energy of molecules at the higher temperatures which result in the separation of molecules and creation of molecular gaps.

(d) Molecular motion: Liquid molecules move randomly in all possible directions however due to small gaps and attractive forces speed of molecules is slower as compared to gas.



Expansion of liquid

2. Name three major kinds of intermolecular forces in liquids. Explain intermolecular forces in HCl.

Ans)

Intermolecular forces in liquids:

1. Diploe-dipole interaction
2. Hydrogen bonding
3. London dispersion forces

Intermolecular forces in HCl: In HCl (hydrochloric acid), intermolecular forces are responsible for the attraction between its molecules. The primary forces at play are dipole-dipole interactions due to the molecule's polarity, as well as London dispersion forces, which occur in all molecules. Dipole-dipole interactions arise from the partial positive and negative charges on hydrogen and chlorine atoms, while London dispersion forces result from temporary fluctuations in electron distribution.

3. Define the following

(a) Molar heat of fusion (b) Molar heat of vapourization (c) Molar heat sublimation

Ans)

(a) Molar heat of fusion (ΔH_{fusion}): It is the amount heat required to convert one mole of a solid completely into liquid at its melting point.

(b) Molar heat of vaporization (ΔH_v): The amount of heat required to convert one mole of a liquid into its vapors at boiling point is referred as molar heat of vaporization.

(c) Molar heat of sublimation (ΔH_s): The amount of heat absorbs when one mole of a solid is directly convert into vapors without going through a liquid state is known as molar heat of sublimation.

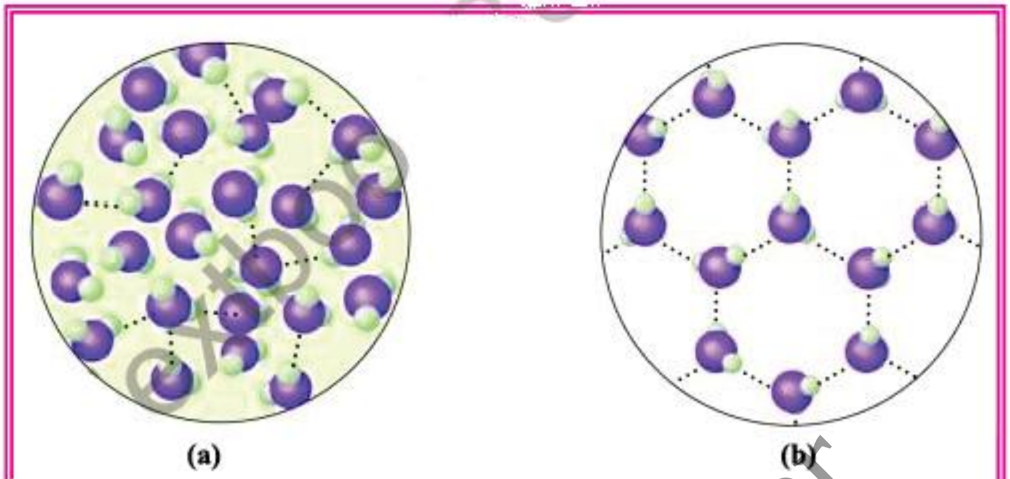
4. Describe hydrogen bonding in water and explain the anomalous behavior of water due to hydrogen bonding.

Ans)

Hydrogen bonding in water: Hydrogen bonding in water is a result of water's polarity, with oxygen attracting electrons more strongly than hydrogen. This leads to the formation of strong hydrogen bonds between water molecules, resulting in several important properties:

1. High specific heat of water
2. High boiling point of water
3. High density of water
4. High viscosity of water
5. High surface tension of water
6. Anomalous behavior of water

Anomalous behavior of water: Hydrogen bondings in water lead to some unusual and unique behavior which is seen in daily life. It shows highest density at 4°C and below this temperature its volume increases instead of decreasing. This anomalous behavior of water can be attributed by arrangement of hydrogen bonding among H_2O molecules.


(a) (b)

Hydrogen bonding in (a) Ice (b) liquid water

Hydrogen bonding in water above 4°C is temporary due to the high thermal energies. Thus water molecules can easily break their hydrogen bond and quickly re-form new hydrogen bonding with some other molecules in the neighborhood.

5. Water is more volatile than glycerin but petrol is more volatile than water at the same temperature. Explain in term of intermolecular force.

Ans) Glycerine has more inter-molecular hydrogen bonds than water for the same number of molecules of each substances. This causes more inter-molecular attraction between Glycerine molecules than Water molecules. As a result, water is more volatile than glycerine. While at the same temperature, petrol (gasoline) is more volatile than water because it is composed of nonpolar hydrocarbons, which have weaker intermolecular forces (London dispersion forces).

6. Give reasons for the following:

i. Water spilled on floor evaporate faster than the same amount of water in a container.

Ans) Spilled water on a floor evaporates faster than the same amount of water in a container due to the larger surface area exposed to the air.

ii. A falling drop of a liquid is spherical.

Ans) A falling drop of liquid forms a spherical shape because of surface tension, which causes the liquid to minimize its surface area and sphere has minimum surface area.

iii. Evaporation is a cooling process.

Ans) Evaporation cools a substance or its surroundings because it absorbs heat energy during the transition from a liquid to a gas, lowering the temperature in the process.

iv. Boiling point of liquid remains constant although heat is continuously supplied to the liquid.

Ans) The boiling point of a liquid remains constant when heat is continuously supplied because the added heat is used to break the intermolecular forces within the liquid, allowing it to change into a gas and not utilized in temperature rise.

v. Mercury has its meniscus upward.

Ans) Mercury exhibits an upward or convex meniscus when placed in a narrow glass tube. This is because the cohesive forces between mercury molecules are stronger than the adhesive forces between mercury and glass, causing the mercury to curve upward at the edges where it meets the glass.

vi. Liquids cannot be compressed as gases do.

Ans) Liquids are generally considered incompressible because they have strong intermolecular forces and molecules that are already close together. Applying pressure to a liquid doesn't significantly change its volume under normal conditions, unlike gases which can be compressed because their molecules are more spread out and have weaker forces between them.

vii. Density of water is highest at 4°C.

Ans) Water achieves its highest density at 4°C due to the unique properties of its molecules and hydrogen bonding. As water cools from higher temperatures to 4°C, hydrogen bonds become optimally balanced, resulting in a maximum packing arrangement. Beyond 4°C, thermal energy disrupts these bonds, causing water to expand and become less dense.

viii. Honey is more viscous than water.

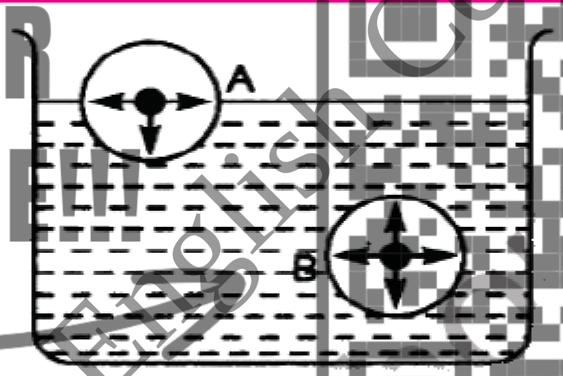
Ans) Honey is more viscous than water due to differences in its molecular structure and intermolecular forces. Honey's larger and more complex molecules create stronger forces that resist flow, making it thicker than water. In contrast, water's simpler molecular structure and weaker intermolecular forces results in lower viscosity.

Descriptive Questions

1. What is Surface tension? Explain it with example. Give its unit and describe the factors that affect on surface tension of liquids?

Ans)

Surface tension: Surface tension is the force acting at right angle on the unit length of surface of liquid.



Cohesive forces in the liquid molecules at surface and inner side

Example: You might have noticed spherical droplets of water coming out of tap for a while just after closing it. The reason behind is the presence of cohesive forces between the surface molecules and the molecules toward the interior side. Since the surface molecules are being pulled by the interior ones, as a consequence, the surface area is reduced as much as possible to acquire a spherical geometry since sphere has the least surface area for a given volume.

Falling drop of a liquid is spherical in shape.

Factors on which surface tension depends:

1. Intermolecular forces: An essential factor which affects on surface tension of liquids is the strength of intermolecular forces. The stronger the intermolecular forces the higher the surface tension. For example surface tension of water is stronger than many other liquids, due to the presence of stronger intermolecular forces (Hydrogen bonds). Mercury has much higher surface tension than water because its atoms are held together by strong metallic bond.
2. Temperature: Surface tension is markedly affected by temperature. High temperature weakens the cohesive forces among the molecules which results in decreasing the surface tension.

2. Explain the factors why honey is more viscous than water?

Ans) Honey is more viscous than water due to several factors:

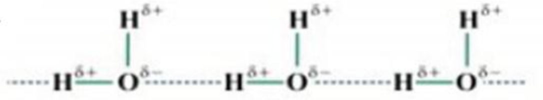
1. **Molecular Size and Structure:** Honey contains larger and more complex molecules, such as sugars like glucose and fructose, which have multiple hydroxyl (-OH) groups. These hydroxyl groups form hydrogen bonds with water molecules, increasing the viscosity of honey.
2. **Hydrogen Bonding:** The presence of numerous hydroxyl groups in honey's molecules allows for extensive hydrogen bonding between the molecules. These hydrogen bonds create strong intermolecular forces that hinder the flow of the liquid, making honey thicker and more viscous.
3. **Additional Components:** Honey also contains other dissolved substances like organic acids, proteins, and small particles. These components further obstruct the movement of water molecules and contribute to the higher viscosity of honey.
4. **Concentration:** The concentration of sugars and other solutes in honey is higher than in water. Higher solute concentrations generally result in higher viscosity because the solute molecules disrupt the flow of the solvent molecules.

3. What is hydrogen bond? How is it established? Give its application in industrial and biochemical process.

Ans) Hydrogen Bonding:

Definition: The force of attraction between partially positive charged hydrogen atom of one molecule and lone pair of electron of highly electronegative atom of another molecule is called Hydrogen bonding.

Formation of hydrogen bond: Hydrogen bonds are formed when a hydrogen atom, bonded to an electronegative atom like oxygen or nitrogen, is attracted to another electronegative atom with lone pairs of electrons. This attraction results in a hydrogen bond, which is a relatively weak but significant intermolecular force.



Application in industrial and biochemical process: Hydrogen bonds have several important applications in both industrial and biochemical processes:

Industrial Applications:

1. **Solvent Properties:** Hydrogen bonds make water an excellent solvent for a wide range of substances, which is crucial in industrial processes like chemical manufacturing, pharmaceuticals, and metallurgy.
2. **Hydration in Chemical Reactions:** In chemical synthesis, hydrogen bonding plays a role in solubilizing and facilitating reactions in aqueous solutions. For example, it's used in the production of various chemicals, including pharmaceuticals and specialty chemicals.
3. **Catalysis:** Hydrogen bonds can influence catalytic processes by helping molecules adopt specific orientations or stabilize transition states. This is valuable in industries involving catalytic reactions, such as the petrochemical industry.

Biochemical Applications:

1. **Protein Structure and Function:** Hydrogen bonds are critical for the three-dimensional structure and stability of proteins. They determine the folding patterns of amino acids and are essential for enzymatic activity and protein-protein interactions.
2. **DNA Structure:** Hydrogen bonds between base pairs (adenine-thymine and cytosine-guanine) stabilize the double helix structure of DNA. Understanding these bonds is fundamental in genetic research, DNA sequencing, and molecular biology.
3. **Enzymatic Reactions:** Hydrogen bonds play a role in enzyme-substrate interactions, helping enzymes bind to their substrates with specificity and facilitating biochemical reactions. This knowledge is applied in various fields, including medicine and biotechnology.
4. **Drug Design:** In pharmaceutical research, understanding the hydrogen bonding interactions between drug molecules and target proteins or nucleic acids is crucial for designing effective drugs and predicting their biological activity.
5. **Biological Membranes:** Hydrogen bonds are involved in the stability and permeability of cell membranes, influencing processes like ion transport, cell signaling, and drug delivery.

4. What is meant by liquid crystals? How is it differing from liquids and crystalline solids?

Ans) Liquid crystals: Liquid crystals are a state of matter that exhibits properties of both liquids and crystalline solids.

Difference between liquid crystals and liquids: Liquid crystals differ from regular liquids in several ways.

- **Molecular Order:** Liquid crystals have partial molecular alignment, whereas liquids have random molecular arrangements.
- **Anisotropy:** Liquid crystals exhibit directional variations in properties, unlike the isotropic nature of most liquids.
- **Responsiveness:** Liquid crystals respond to external factors like temperature, pressure, and electric fields, altering their molecular arrangement and optical properties.
- **Phases:** Liquid crystals can exist in different phases, each with unique molecular arrangements and optical characteristics.
- **Viscosity:** Liquid crystals often have higher viscosity compared to regular liquids due to partial molecular alignment.
- **Electro-optical Properties:** Liquid crystals can change their optical properties in response to an electric field, a crucial feature for applications like LCDs.

Difference between liquid crystals and crystalline solids: Liquid crystals differ from crystalline solids in several ways.

- **Molecular Arrangement:** Liquid Crystals have partial molecular order and alignment, but not as regular or long-range as in crystalline solids.
- **Fluidity:** Liquid crystals are fluid and can flow and change shape, like regular liquids. Crystalline solids are rigid, maintain structural integrity, and do not flow.
- **Phase Transitions:** Liquid crystals can change phases in response to external factors, altering molecular arrangement and optical properties. While crystalline solids remain in a fixed phase under normal conditions, undergoing phase transitions only under extreme conditions.
- **Optical Properties:** Liquid crystals are exhibits optical properties sensitive to molecular orientation, allowing for manipulation of transparency and refractive index. Crystalline solids have well-defined and unchanging optical properties determined by the crystal lattice.

- **Range of Order:** Liquid crystals are partial molecular order over short distances, with molecules aligned in preferred directions. Crystalline solids are long-range order, with molecules or atoms arranged in a repeating and extended lattice structure.

Chapter 6: STATE OF MATTER III: SOLIDS

Multiple Choice Questions

1. Choose the correct answer:

(i) Quantity of energy released when I mole of the ionic crystal is formed from the gaseous ions is called:

(a) Bond energy (b) Potential energy

(c) Ionization energy (d) Lattice energy

(ii) Graphite can conduct electricity in one direction only. With this behavior, it is said to be:

(a) Amorphous (b) Symmetrical

(c) Anisotropic (d) Polymorphous

(iii) NaCl and MgO are isomorphous solids because these have same:

(a) Melting point (b) Boiling point

(c) Geometrical shapes (d) Chemical Properties

(iv) The temperature at which two allotropic forms co-exist in equilibrium is called as:

(a) Melting temperature (b) Fusion temperature

(c) Transition temperature (d) Critical temperature

(v) Diamond is the example of:

(a) Ionic solid (b) Covalent solid

(c) Metallic solid (d) Molecular solid

(vi) Ice is a molecular solid, the intermolecular force of attraction among its molecules are:

(a) Ionic bond (b) Covalent bond

(c) Metallic bond (d) Hydrogen bond

(vii) If all three axes in unit cell are of different length but all angles are of 90° then it is identified as:

(a) Orthorhombic system (b) Cubic system

(c) Tetragonal system (d) Hexagonal system

(viii) In NaCl, cach Na^+ ion is surrounded by Cl^- ions in the numbers:

(a) Four (b) Three

(c) Six (d)Seven

(ix) It is an example of crystalline solid:

(a) Alum (b) Glass

(c) Plastic (d) Rubber

(x) Each unit cell of sodium chloride consists of

(a) Eight Na^+ and Eight Cl^- ions (b) Two Na^+ and Two Cl^- ions

(c) Four Na^+ and Four Cl^- ions (d) Four Na^+ and Six Cl^- ions

KEY:

i. d	ii. c	iii. c	iv. c	v. b
vi. d	vii. a	viii. c	ix. a	x. c

Short Questions

1. Define the following terms:

(1) Allotropy (2) Sublimation (3) Melting point (4) Unit cell

Ans)

(1) Allotropy: Allotropy, also known as allotropism, is a phenomenon in chemistry where an element can exist in multiple structural forms or arrangements in the same physical state.

(2) Sublimation: Some solids directly change into vapours on heating without passing through liquid phase, which is known as sublimation.

(3) Melting point: The melting point of a substance is the temperature at which it changes from a solid state to a liquid state at a given pressure.

(4) Unit cell: The smallest repeating pattern from which the lattice is built is known as unit cell.

2. Define anisotropy. Which type of solids have this property?

Ans)

Anisotropy: A very unique behavior of crystalline solid is the variation in certain physical properties (Refractive index, Coefficient of thermal expansion, Electrical and Thermal conductivity) along different directions in the crystal lattice. This phenomenon is known as anisotropy.

- Crystalline solids have this property.

3. What is Transition temperature? Explain with examples.

Ans)

Transition temperature:

Definition: A transition temperature, also known as a critical temperature, is a specific temperature at which a material undergoes a significant change in its properties.

Examples: Examples include the melting point (solid to liquid transition) in substances like water, the Curie temperature (magnetic transition) in ferromagnetic materials like iron, the superconducting transition temperature (zero electrical resistance) in materials like mercury, the glass transition temperature (rigid to flexible transition) in glass and certain polymers, and order-disorder transition temperatures in shape memory alloys. Transition temperatures are important for understanding and utilizing the behavior of materials in various applications.

4. Explain why diamond is non-conductor of electricity and Graphite is a conductor.

Ans) Diamond is a non-conductor of electricity because it has a three-dimensional structure with strong covalent bonds, leaving no free electrons for electrical conduction. In contrast, graphite is a conductor because its layered structure allows for delocalized or free-moving electrons between the layers, facilitating electrical conduction. The difference in electrical conductivity between these two forms of carbon is primarily due to their atomic structures and the presence of delocalized electrons in graphite.

5. Define lattice energy. Explain how it is effected by size and the charge of ion.

Ans) Lattice Energy: The quantity of energy released when one mole of the Ionic crystal is formed from the gaseous ions.

1. **The size of cation or anion:** The lattice energy decreases with the increase in the size of cation or anion. The reason in both cases is the same. The smaller the size of cation or anion the closer the packing of oppositively charged ions and thus require high energy to break the lattice and convert the solid into isolated ions. For example lattice energy of NaF (923 KJ/mol) is higher than KF (821 KJ/mol) because of smaller ionic radii of Na$^+$ than K$^+$ ion. The smaller ionic size of Na$^+$ ion makes the packing more closely and thus need relatively high lattice energy for the separation of ions.
2. **Charge of ion:** Lattice energy also affected by the charge of ion. The greater the charge of ion the higher is the lattice energy. For example lattice energy of BeF$_2$ (3505 KJ/mol) is much higher than LiF (1036) because Lithium possess +1 charge in LiF where as the charge of Beryllium is +2 in BeF$_2$.

6. Differentiate between the following:

(i) Crystalline and amorphous solids **(ii) Isomorphism and polymorphism**

Ans)

(i)

Crystalline	Amorphous
They exist in definite geometrical shape	They don't have definite shape
They have sharp melting points	They melt over a wide range of temperatures
They show anisotropic behavior that is properties like mechanical strength, refractive index and electrical conductivity depend upon direction.	They are isotropic in nature.
They can be cut down at fixed cleavage plane	When they are cut or hammered cause in irregular fracture.

(ii)

Isomorphism	Polymorphism
Isomorphism refers to the similarity in crystal structures of different substances or compounds.	Polymorphism refers to the ability of a single substance to exist in multiple crystal structures or forms.
It involves different substances or compounds having similar atomic arrangements.	It involves a single substance having different crystal structures.
There are various types of isomorphism, such as complete isomorphism and partial isomorphism, depending on the extent of similarity in crystal structures.	Polymorphism is typically classified into two main types: monotropic polymorphism (stable under all conditions) and enantiotropic polymorphism (interconvertible with changes in temperature or pressure).
Examples include minerals like feldspar, where different elements (e.g., potassium, sodium, calcium) can replace each other in the crystal structure without altering the structure.	Examples include substances like carbon, which can exist in various forms like diamond and graphite, each with a different crystal structure.

7. Explain the following with scientific reason.

(i) Why the compressibility of solids is nearly zero?

Ans) Solids have nearly zero compressibility because they possess strong intermolecular forces, maintain highly ordered lattice structures, and have bonds that are already at their minimum energy state. These factors make it extremely resistant to changes in volume when subjected to external pressure.

(ii) Why some solids are sublime in nature?

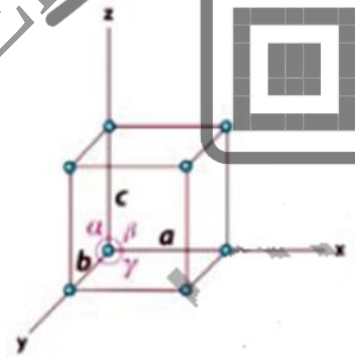
Ans) Certain solids undergo sublimation, transitioning directly from the solid to the gas phase, due to factors like weak intermolecular forces, low triple point temperatures, high vapor pressures at lower temperatures, and the endothermic nature of the sublimation process.

Descriptive Questions

1. Define unit cell. Draw a diagram to show its axial distances and axial angles.

Ans) Unit Cell: The smallest repeating pattern from which the lattice is built is known as unit cell.

Diagram: The shape of a unit cell is associated with three axial distance named as (a, b and c) and three axial angles named as (α, β and γ).

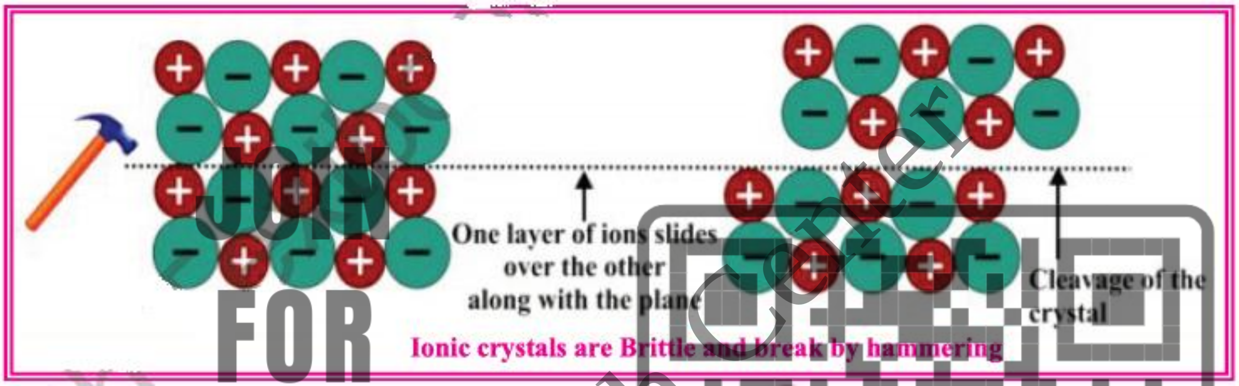


Dimensions of unit cell

2. Give four properties of ionic solids. How can you determine the number of Na$^+$ and Cl$^-$ ions in a unit cell of sodium chloride?

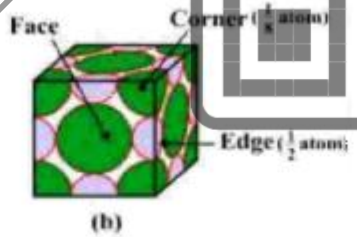
Ans) Properties: Some properties of ionic crystals are described here.

1. They are hard at room temperature due to the presence of strong electrostatic forces attraction.
2. They are brittle and can be shatter easily by hammering.



3. They possess high melting point.
4. They are soluble in water and similar polar solvent.

Number of Na$^+$ and Cl$^-$ ions in a unit cell of sodium chloride:



Portion of atoms in the unit cubic cell

Chloride (Cl$^-$) ion determination: Above figure reveals that eight (8) chloride ions are located at the eight corners of cube while six (6) chloride ions (Cl$^-$) at the center of its six faces. On the basis of this information, one can determine the number of Cl$^-$ ions in each unit cell of sodium chloride crystal.

Since each chloride ion (Cl$^-$) at the corner is shared between eight other unit cells thus, its share to each unit cell should be $\frac{1}{8}$ therefore, No. of chloride (Cl^-) ions at the corner of one unit cell = $\frac{1}{8}$ x 8=1.

On the other hand six faces possess six chloride ions at their center but each face share with two unit cells therefore.

No. of chloride (Cl^-) ions at face center = $\frac{1}{2}$ x 6 = 3

Total no. of chloride ions in each unit cell = 1 + 3 = 4.

Sodium (Na^+) ion determination: There are 12 edges of cube, each contains one sodium ion (Na^+). Also each Na^+ ion on the edge of cube is shared by four (4) unit cells therefore.

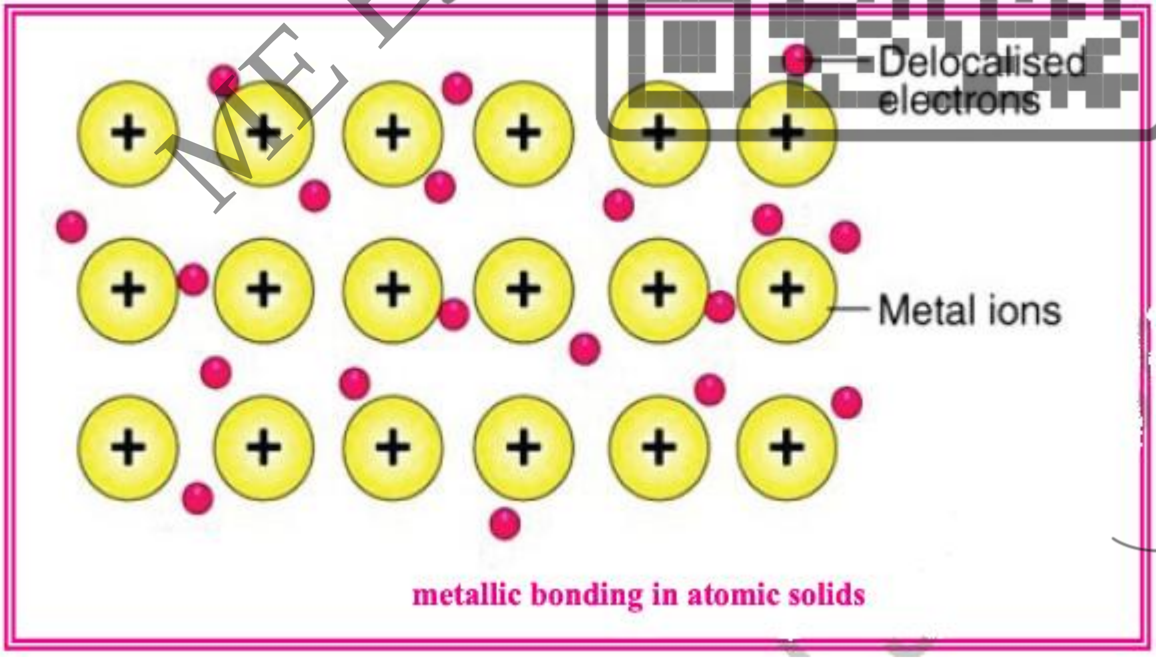
No. of Na^+ ions on each edge = $\frac{1}{4}$ x 12 = 3.

No. of Na^+ ion on the center of unit cell = 1.

Total Na^+ ion in each unit cell = 3+1= 4.

3. Give a brief account on metallic solids. Why they conduct heat and electricity?

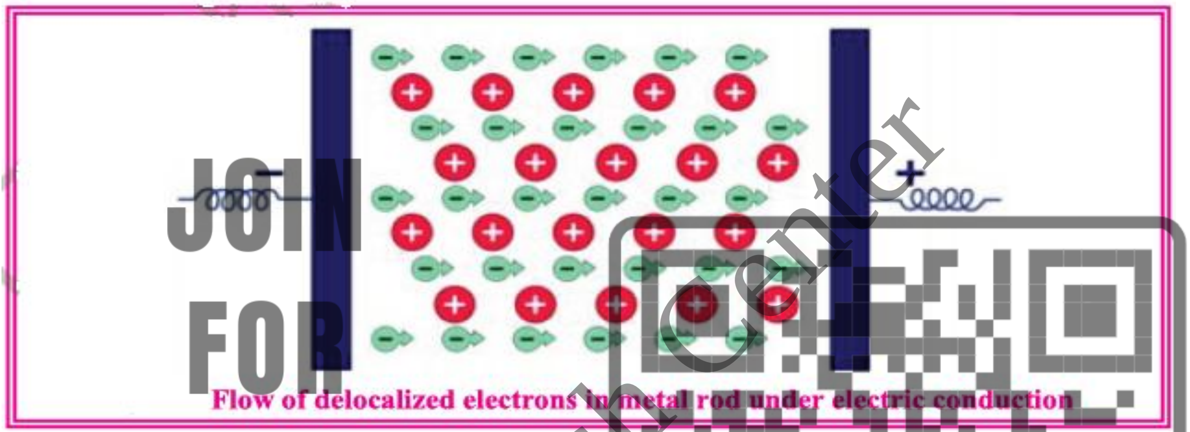
Ans) Metallic Solids: Particles of metallic crystals are metal atoms. According to electron sea theory, metal atoms lose their all valence electrons into the vacant spaces and become positively charged metal ions. These positive charged metal ions arranged themselves in a three dimensional crystal lattice and bonded with sea of electrons.



metallic bonding in atomic solids

Characteristics properties: Some characteristics properties of metallic solids are described below.

1. Metallic solids are identified by their malleability and ductility.
2. Metallic solids are looks like dull but when freshly cut, the inner layer appear shiny. This property is known as metallic luster.
3. The electrical conductivity of metallic solids is due to the free movement of delocalized electron in electric field.



Flow of delocalized electrons in metal rod under electric conduction

4. Metals are good conductor of heat. Thus when a rod of metal is heated from one of its terminal, the free electrons of metal absorb heat and hence their kinetic energy increases. These free electrons then tends move towards the other end of the rod which is relatively cooler.

Conduction of heat and electricity: Metallic solids conduct heat and electricity because they have a unique electron structure. Valence electrons in metals are free to move throughout the material, creating a "sea" of free electrons. This electron mobility, along with the delocalization of electrons across the lattice, results in low electrical resistance and efficient heat conduction. As a result, metals are excellent conductors of both heat and electricity.

4. What is meant by polymorphism? How it is related to allotropy. Give your answer with examples.

Ans) Polymorphism: The phenomenon in which a substance under different conditions can exist in more than one crystalline structure is known as polymorphism.

Relation between allotropy and polymorphism: Allotropy is limited to pure elements only. It defines as "The existence of the same elements in two or more different crystal structures having the same chemical nature but different physical properties". Polymorphism is defined in this manner as well.

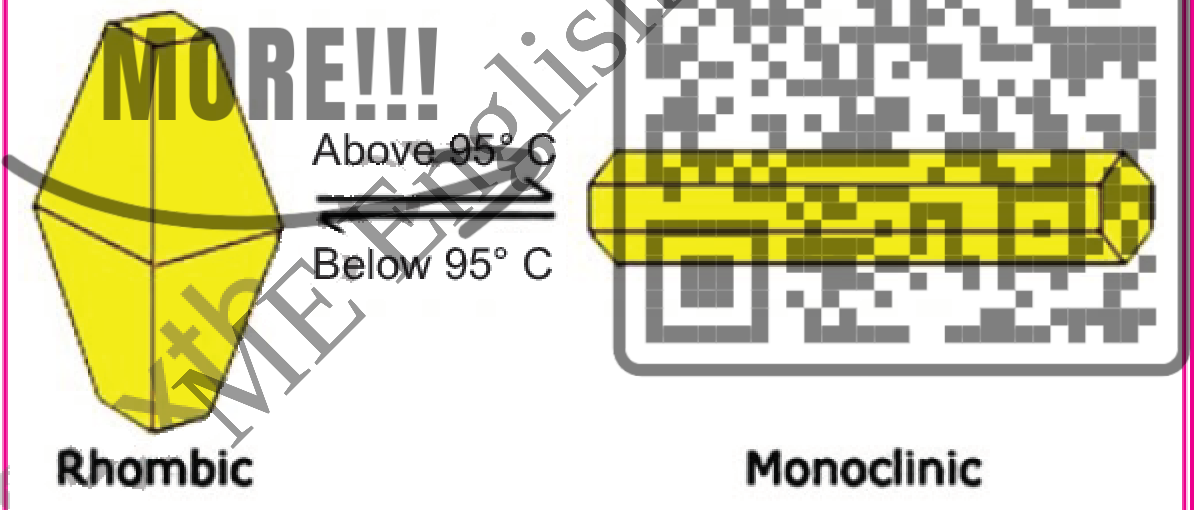
Example 1: Carbon exists in two crystalline allotropic forms one is called Diamond which has a cubic geometry while other is Graphite in which the geometry of crystal is hexagonal.

Example 2: The two important crystalline allotropic forms of sulphur are:

1. Rhombic sulphur (α-sulphur)
2. Monoclinic sulphur (β-sulphur)

Rhombic sulphur is a yellow octahedral crystalline form. It is stable at ordinary temperature but when heated gently above 95.5°C, it change into monoclinic sulphur. The transition temperature of Rhombic and monoclinic sulphur is 95.5°C.

$$\text{Rhombic Sulphur} \xrightleftharpoons{95.5^\circ\text{C}} \text{Monoclinic Sulphur}$$



Rhombic and monoclinic sulphur at transition temperature

5. Molecular solids are soft and possess low melting point, how can you justify this statement.

Ans) The statement that molecular solids are soft and possess low melting points can be justified based on the characteristics of molecular solids:

1. **Weak Intermolecular Forces:** Molecular solids are composed of individual molecules held together by relatively weak intermolecular forces, such as London dispersion forces (Van der Waals forces), dipole-dipole interactions, and hydrogen bonds. These forces are much weaker than the strong covalent or metallic bonds found in other types of solids.
2. **Low Melting Points:** Because the intermolecular forces in molecular solids are weak, it takes relatively little energy to overcome these forces and transition the solid into a liquid. As a result, molecular solids generally have low melting points compared to other types of solids. The weak forces can be easily disrupted by an increase in temperature, causing the solid to melt.
3. **Softness:** Molecular solids also tend to be soft because the weak intermolecular forces allow the individual molecules to slide past each other relatively easily. This lack of strong bonding between molecules means that they can be readily displaced when an external force is applied, resulting in a soft or easily deformable texture.

Chapter 7: CHEMICAL EQUILIBRIUM

Multiple Choice Questions:

1. Choose the correct answer

(i) In the equilibrium system of $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, the correct relationship between Ke and Kp is:

(a) Kp > Kc (b) Kp < Kc (c) Kp = Kc (d) $\frac{K_p}{K_c} = 1$

(ii) The equilibrium of which of the following reaction would not be affected by an increase in pressure:

(a) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ (b) $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$

(c) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

(iii) What happens to the value of Kc when a catalyst is added to a chemical system at equilibrium?

(a) It decreases (b) It increases

(c) It becomes zero (d) It remains unchanged

(iv) The correct Ksp expression of a sparingly soluble salt $Li_2C_2O_4$ among the following is:

(a) $Ksp=[Li^+][C_2O_4^{-2}]$ (b) $Ksp=[Li^+]^2[C_2O_4^{-2}]$

(c) $Ksp=[2Li^+][C_2O_4^{-2}]$ (d) $Ksp=[2Li^+]^2[C_2O_4^{-2}]^2$

(v) If the equilibrium expression of a reversible reaction is

$$Kc= \frac{[C]^2}{[A][B]}$$

The balanced equilibrium equation should be:

(a) $C \rightleftharpoons A+B$ (b) $A+B \rightleftharpoons C$

(c) $2C \rightleftharpoons A+B$ (d) $A+B \rightleftharpoons 2C$

(vi) The equilibrium of $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (ΔH= +ve) is affected by change in:

(a) Temperature only (b) Pressure only

(c) Both temperature and pressure (d) Neither temperature nor pressure

(vii) In the reaction $A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$, the equilibrium constants Kp = Kc because:

(a) $\Delta n > 1$ (b) $\Delta n < 1$ (c) $\Delta n = 1$ (d) $\Delta n = 0$

(viii) The term active mass use in law of mass action means:

(a) No. of mole (b) No. of molecules (c) mole per dm^3 (d) gram per dm^3

(ix) NaCl when added to an aqueous silver chloride solution:

(a) Decreases the solubility of AgCl (b) Increases the solubility of AgCl

(e) Forms a clear solution (d) Does not effect

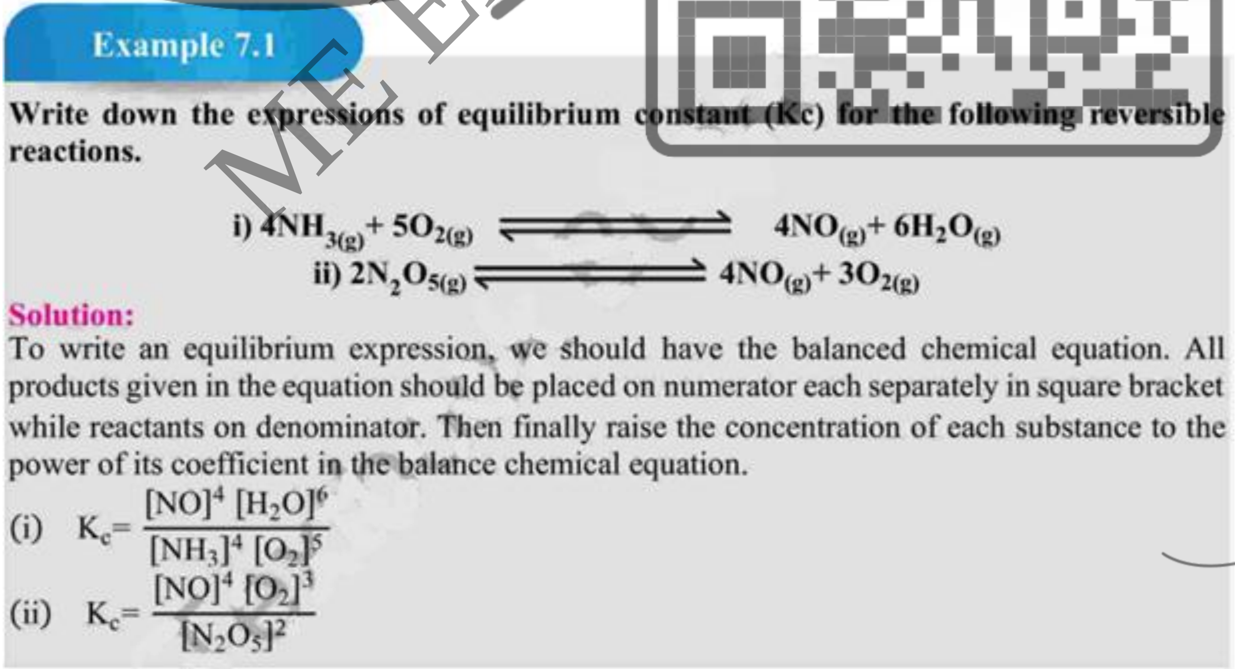
(x) Some reactions are nearly to completion in the forward direction and identified by their

(a) Very high value of Kc (b) Very low value of Kc

(c) Very high value of ΔH (d) Very low value of ΔH

Key:

i. a	ii. c	iii. d	iv. b	v. d
vi. a	vii. d	viii. c	ix. a	x. a



Example 7.1

Write down the expressions of equilibrium constant (Kc) for the following reversible reactions.

$$\text{i) } 4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$$

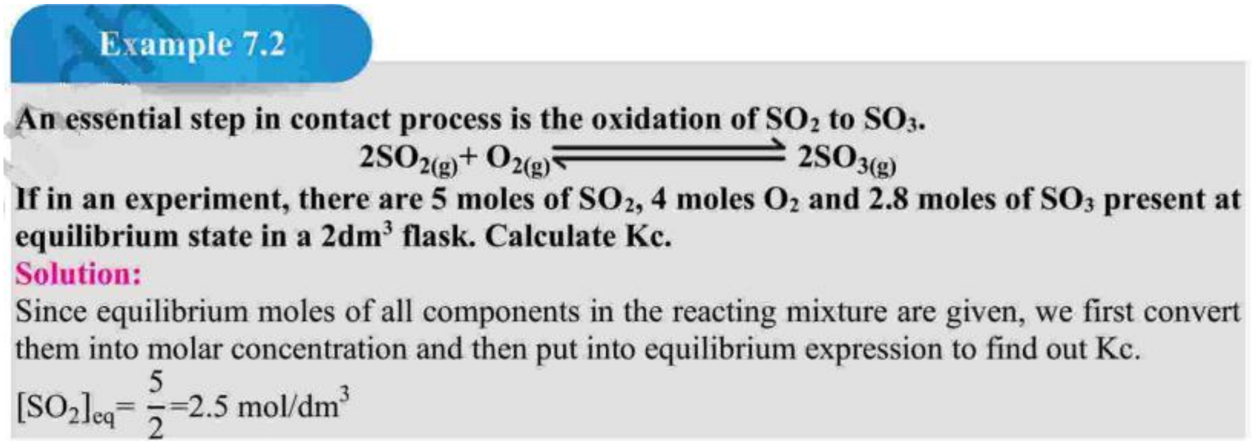
$$\text{ii) } 2N_2O_{5(g)} \rightleftharpoons 4NO_{(g)} + 3O_{2(g)}$$

Solution:

To write an equilibrium expression, we should have the balanced chemical equation. All products given in the equation should be placed on numerator each separately in square bracket while reactants on denominator. Then finally raise the concentration of each substance to the power of its coefficient in the balance chemical equation.

$$\text{(i)} \quad K_c = \frac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^5}$$

$$\text{(ii)} \quad K_c = \frac{[NO]^4\,[O_2]^3}{[N_2O_5]^2}$$



Example 7.2

An essential step in contact process is the oxidation of SO_2 to SO_3.

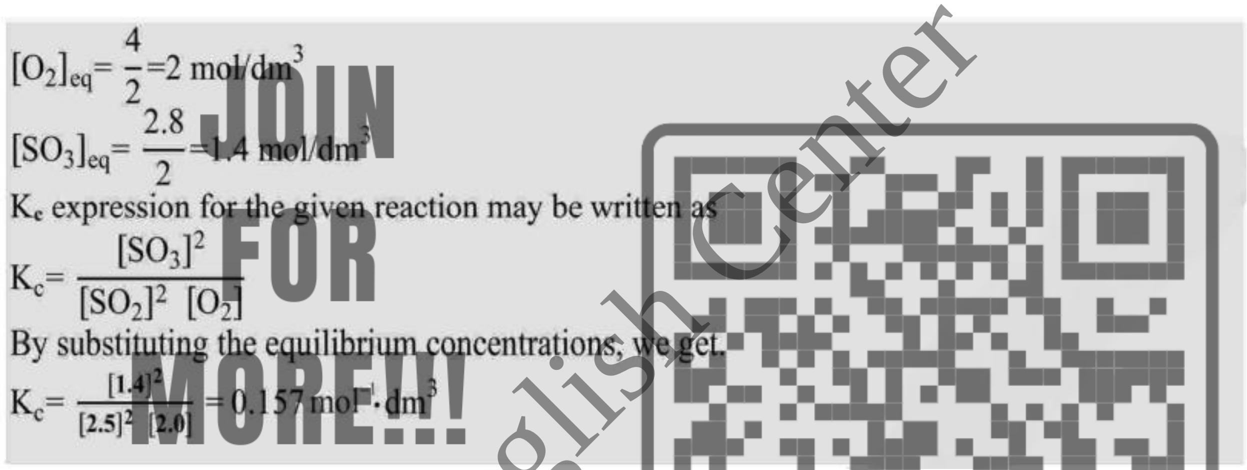
$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

If in an experiment, there are 5 moles of SO_2, 4 moles O_2 and 2.8 moles of SO_3 present at equilibrium state in a $2dm^3$ flask. Calculate Kc.

Solution:

Since equilibrium moles of all components in the reacting mixture are given, we first convert them into molar concentration and then put into equilibrium expression to find out Kc.

$$[SO_2]_{eq} = \frac{5}{2} = 2.5\ mol/dm^3$$



$$[O_2]_{eq} = \frac{4}{2} = 2\ mol/dm^3$$

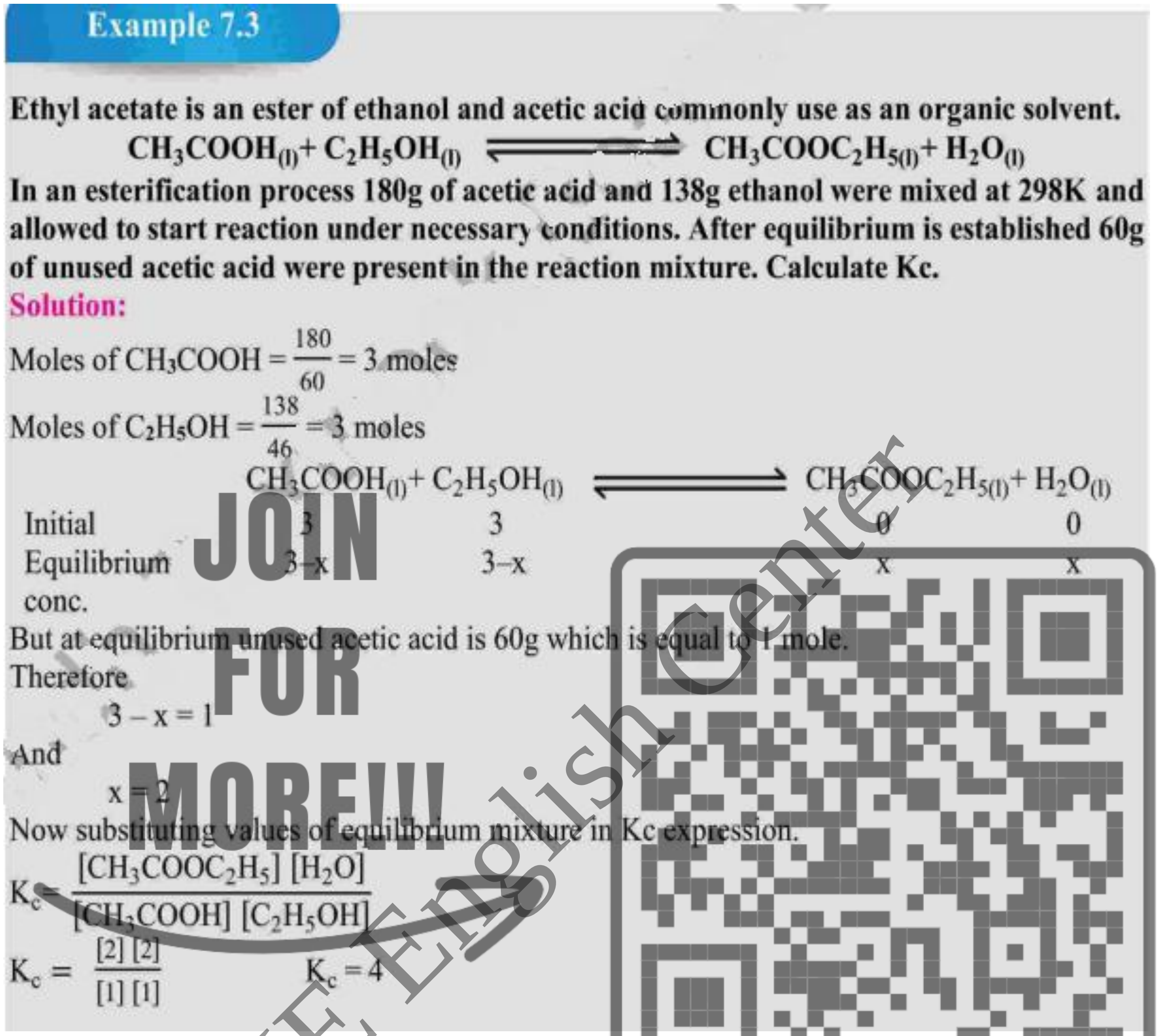
$$[SO_3]_{eq} = \frac{2.8}{2} = 1.4\ mol/dm^3$$

K_c expression for the given reaction may be written as

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]}$$

By substituting the equilibrium concentrations, we get.

$$K_c = \frac{[1.4]^2}{[2.5]^2\ [2.0]} = 0.157\ mol^{-1} \cdot dm^3$$



Example 7.3

Ethyl acetate is an ester of ethanol and acetic acid commonly use as an organic solvent.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

In an esterification process 180g of acetic acid and 138g ethanol were mixed at 298K and allowed to start reaction under necessary conditions. After equilibrium is established 60g of unused acetic acid were present in the reaction mixture. Calculate Kc.

Solution:

Moles of $CH_3COOH = \frac{180}{60} = 3$ moles

Moles of $C_2H_5OH = \frac{138}{46} = 3$ moles

	$CH_3COOH_{(l)}$ +	$C_2H_5OH_{(l)}$	$\rightleftharpoons$	$CH_3COOC_2H_{5(l)}$ +	$H_2O_{(l)}$
Initial	3	3		0	0
Equilibrium conc.	3–x	3–x		x	x

But at equilibrium unused acetic acid is 60g which is equal to 1 mole.

Therefore

$3 - x = 1$

And

$x = 2$

Now substituting values of equilibrium mixture in Kc expression.

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$K_c = \frac{[2]\,[2]}{[1]\,[1]} \qquad K_c = 4$$

Example 7.4

Nitrosyl chloride is a yellow coloured gas prepared by the reaction of NO and Cl_2 gases.

$$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$$

If at certain temperature, the partial pressure of equilibrium mixture is NO = 0.17 atm, Cl_2 = 0.2 atm and NOCl = 1.4 atm, Calculate Kp

Solution:

The equilibrium expression of the given reaction is written as

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2\ (P_{Cl_2})}$$

Substituting the partial pressure in equilibrium expression, we get

$$K_p = \frac{(1.4)^2}{(0.17)^2\ (0.2)} \qquad K_p = 339.1$$

Example 7.5

Kc for the given reaction at certain temperature is 2.72.

$$A + 3B \rightleftharpoons 2C$$

If in a $5dm^3$ reaction vessel the reaction mixture contains 8 moles A, 6 moles B, and 5 moles C. Predict whether the reaction is in equilibrium, if not what is the direction of net reaction?

Solution:

To find the answer, we first need to know what is the numerical value of Qc. It will be determined by substituting the values of conc. of A, B and C in reaction quotient expression then compare it with Kc. The relative values of Qc and Kc tells us whether the reaction is at equilibrium or proceed in a particular direction for getting equilibrium.

The molar concentrations of A, B and C can be calculated as

$$[A] = \frac{8}{5} = 1.6\ mol/dm^3$$

$$[B] = \frac{6}{5} = 1.2\ mol/dm^3$$

$$[C] = \frac{5}{5} = 1\ mol/dm^3$$

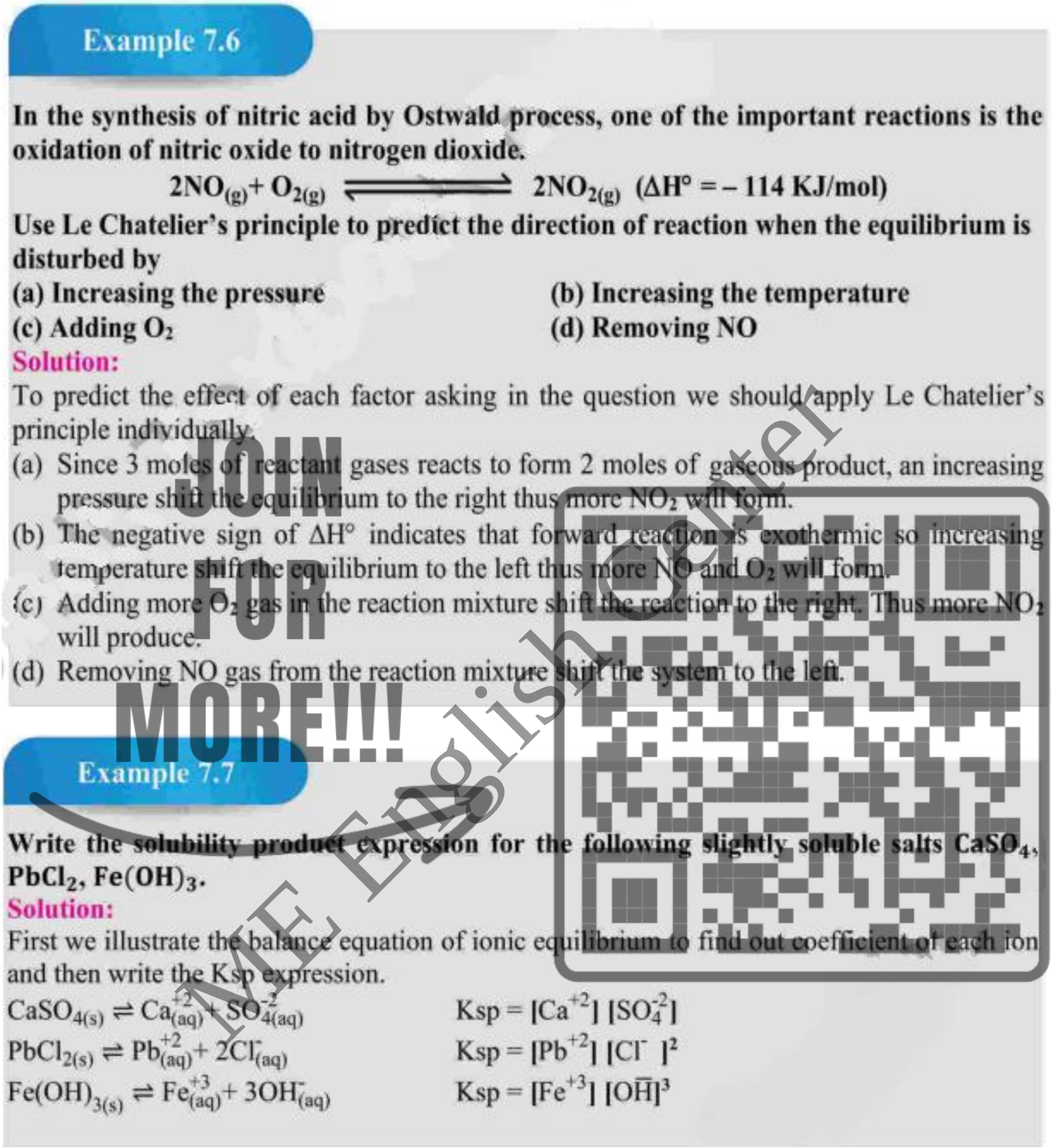
Qc expression of the reaction is written as

$$Qc = \frac{[C]^2}{[A]\ [B]^3}$$

Substituting these values in reaction quotient

$$Qc = \frac{(1)^2}{(1.6)\ (1.2)^3} = 0.36$$

Since Qc < Kc, the reaction mixture is not at equilibrium but proceed from left to right to increase the concentration or product.



Example 7.6

In the synthesis of nitric acid by Ostwald process, one of the important reactions is the oxidation of nitric oxide to nitrogen dioxide.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad (\Delta H^\circ = -114\ KJ/mol)$$

Use Le Chatelier's principle to predict the direction of reaction when the equilibrium is disturbed by

(a) Increasing the pressure **(b) Increasing the temperature**

(c) Adding O_2 **(d) Removing NO**

Solution:

To predict the effect of each factor asking in the question we should apply Le Chatelier's principle individually.

(a) Since 3 moles of reactant gases reacts to form 2 moles of gaseous product, an increasing pressure shift the equilibrium to the right thus more NO_2 will form.

(b) The negative sign of ΔH° indicates that forward reaction is exothermic so increasing temperature shift the equilibrium to the left thus more NO and O_2 will form.

(c) Adding more O_2 gas in the reaction mixture shift the reaction to the right. Thus more NO_2 will produce.

(d) Removing NO gas from the reaction mixture shift the system to the left.

Example 7.7

Write the solubility product expression for the following slightly soluble salts $CaSO_4$, $PbCl_2$, $Fe(OH)_3$.

Solution:

First we illustrate the balance equation of ionic equilibrium to find out coefficient of each ion and then write the Ksp expression.

$CaSO_{4(s)} \rightleftharpoons Ca^{+2}_{(aq)} + SO^{-2}_{4(aq)}$ Ksp = $[Ca^{+2}]\ [SO_4^{-2}]$

$PbCl_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^{-}_{(aq)}$ Ksp = $[Pb^{+2}]\ [Cl^{-}]^2$

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{+3}_{(aq)} + 3OH^{-}_{(aq)}$ Ksp = $[Fe^{+3}]\ [\overline{OH}]^3$

Example 7.8

Silver sulphate (Ag_2SO_4) is used for medicinal purpose to fill wounds. Its solubility in water at 25°C is 1.43×10^{-2} mol/dm³. What will be its Ksp.

Solution:

First write a net ionic equation of Ag_2SO_4 to note the number of coefficient of each ion. Then put the values of ionic concentration in ksp expression.

$$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + SO^{-2}_{4(aq)}$$

The ionic concentrations of 2 moles Ag^+ and 1 mol SO_4^{-2} are illustrated as

$[Ag^+] = 2 \times 1.43 \times 10^{-2} = 2.86 \times 10^{-2}$ mol/dm³

$[SO_4^{-2}] = 1.43 \times 10^{-2}$ mol/dm³

Now inserting these values in ksp expression

$Ksp = [Ag^+]^2 [SO_4^{-2}]$

$Ksp = [2.86 \times 10^{-2}]^2 [1.43 \times 10^{-2}]$

$Ksp = 1.17 \times 10^{-5}$ mol³/dm⁹

Example 7.9

The Ksp of $Zn(OH)_2$ is 2.1×10^{-16} mol³/dm⁹ at 25°C. Calculate its solubility in g/dm³. (The atomic mass of Zn = 65.4)

Solution:

This problem is exactly reverse from previous one. Here we are given with the value of Ksp and the task is to find out solubility in g/dm³. Making the strategy, first write the Ksp expression in which ionic concentration will be written in term of 'S' then calculate molar solubility from known Ksp value. Finally convert it into g/dm³ by multiplying it with molecular mass of $Zn(OH)_2$.

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2OH^{-}_{(aq)}$$

$Ksp = [Zn^{+2}] [OH^-]^2$

Since there are two hydroxide ions for every zinc ion, we may rewrite the expression as

$Ksp = [X] [2X]^2$

$Ksp = 4x^3$

$2.1 \times 10^{-16} = 4x^3$

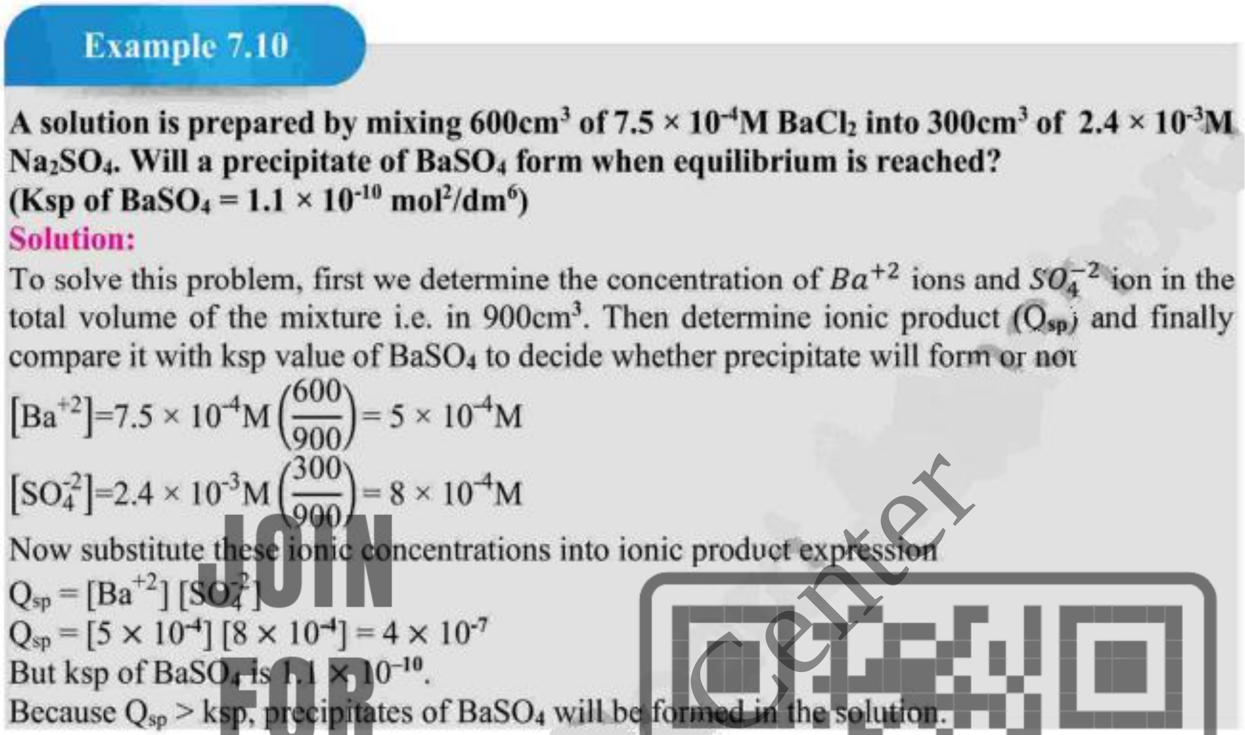
$$\frac{2.1 \times 10^{-16}}{4} = X^3$$

$X = 3.74 \times 10^{-6}$ mol/dm³

To get the solubility in gram/dm³, find the molecular mass of $Zn(OH)_2$ which is

$65.4 + 32 + 2 = 99.4$

$$\text{Solubility} = \frac{3.74 \times 10^{-6}\text{mol}}{\text{dm}^3} \times \frac{99.4\text{g}}{\text{mol}} = 3.717 \times 10^{-4}\text{g/dm}^3$$



Example 7.10

A solution is prepared by mixing 600cm^3 of 7.5×10^{-4}M $BaCl_2$ into 300cm^3 of 2.4×10^{-3}M Na_2SO_4. Will a precipitate of $BaSO_4$ form when equilibrium is reached?
(Ksp of $BaSO_4 = 1.1 \times 10^{-10}$ mol^2/dm^6)

Solution:

To solve this problem, first we determine the concentration of Ba^{+2} ions and SO_4^{-2} ion in the total volume of the mixture i.e. in 900cm^3. Then determine ionic product (Q_{sp}) and finally compare it with ksp value of $BaSO_4$ to decide whether precipitate will form or not

$$[Ba^{+2}] = 7.5 \times 10^{-4}M\left(\frac{600}{900}\right) = 5 \times 10^{-4}M$$

$$[SO_4^{-2}] = 2.4 \times 10^{-3}M\left(\frac{300}{900}\right) = 8 \times 10^{-4}M$$

Now substitute these ionic concentrations into ionic product expression

$Q_{sp} = [Ba^{+2}]\,[SO_4^{-2}]$

$Q_{sp} = [5 \times 10^{-4}]\,[8 \times 10^{-4}] = 4 \times 10^{-7}$

But ksp of $BaSO_4$ is 1.1×10^{-10}.

Because Q_{sp} > ksp, precipitates of $BaSO_4$ will be formed in the solution.

Short Questions

1. Define the following:

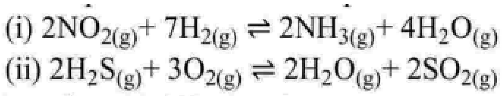
(i) Reversible reaction **(ii) Chemical equilibrium**

Ans)

(i) Reversible reaction: In some chemical reactions, the products of the reaction can react together to produce the original reactants .These reactions are called reversible reactions.

(ii) Chemical equilibrium: Chemical equilibrium is a state in a reversible reaction where no net change in the concentration of reactants and products occur with time.

2. Write expression of Kc and Kp for the following reversible reactions.



(i) $2NO_{2(g)} + 7H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 4H_2O_{(g)}$

(ii) $2H_2S_{(g)} + 3O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2SO_{2(g)}$

Ans)

(i)

Kc = $\frac{[NH_3]^2[H_2O]^4}{[NO_2]^2[H_2]^7}$

Kp = $\frac{(P_{NH_3})^2(P_{H_2O})^4}{(P_{NO_2})^2(P_{H_2})^7}$

(ii)

Kc = $\frac{[H_2O]^2\ [SO_2]^2}{[H_2S]^2[O_2]^3}$

Kp = $\frac{(P_{H_2O})^2(P_{SO_2})^2}{(P_{H_2S})^2(P_{O_2})^3}$

3. (a) Define solubility product.

(b) Write the solubility product expression of the following salts.

BaF_2 , $Li_2C_2O_4$, $MgCO_3$, Ag_3PO_4

Ans)

(a) Solubility product: Solubility product (Ksp) of a sparingly soluble salt may define as "the product of molar concentration of its positive and negative ions each raised to the power of its coefficient in ionized equilibrium equation".

(b) First we illustrate the balance equation of ionic equilibrium to find out coefficient of each ion and then write the Ksp expression

$BaF_2(s) \leftrightharpoons Ba^{+2}\ (aq) + 2F^{-}\ (aq)$	Ksp = $[Ba^{+2}]\ [F^{-}]^2$
$Li_2C_2O_4(s) \rightleftharpoons 2Li^{+}(aq) + C_2O_2^{-4}(aq)$	Ksp = $[Li^{+}]^2\ [C_2O_2^{-4}]$

$MgCO_3(s) \rightleftharpoons Mg^{+2}(aq) + CO_3^{-2}(aq)$ $K_{sp} = [Mg^{+2}][CO_3^{-2}]$

$Ag_3PO_4(s) \rightleftharpoons 3Ag^{+}(aq) + PO_4^{-3}(aq)$ $K_{sp} = [Ag^{+}]^3[PO_4^{-3}]$

4. Using Le-Chatelier's principle, explain three ways in which yield of SO_3 can be increased in Contact process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad (\Delta H^\circ = -ve)$$

Ans)

(i) Effect of Concentration: If more sulphur di oxide (SO_2) or oxygen (O_2) is added at equilibrium, according or Le- Chatelier's principle, the equlibrium is shift towards forward direction to reduce concentration of Sulphur dioxide (SO_2) or oxygen (O_2) and as a result of this concentration of Sulphur tri oxide (SO_3) is increases.

(ii) Effect of Temperature: Formation of SO_3, is an exothermic reaction. If, at equilibrium, temperature is decreases than according to Le-Chatelier's principle, the equilibrium shifts towards forward direction and more amount of SO_3, is produced.

(iii) Effect of Pressure: Since, formation of SO_3 is take place by decrease in volume therefore when pressure is increased the equilibrium is shift towards forward direction and as a result of this more SO_3 is produced.

Descriptive Questions

1. State Law of mass action and derive Kc expression of a general reversible reaction.

Ans) Law of mass action: 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 reactants.

Derivation for expression of equilibrium constant (Kc): Consider a general reversible reaction in which reacting species A, B, C and D exists in equilibrium state at a certain temperature.

$$aA + bB \rightleftharpoons cC + dD$$

According to the law of mass action, the rate of forward reaction (R_f) is directly proportional to the product of active masses of A and B.

$$R_f \propto [A]^a [B]^b \quad \text{or} \quad R_f = K_f [A]^a [B]^b$$

Similarly the rate of backward reaction (R_b) is directly proportional to the active masses of C and D

$$R_b \propto [C]^c\,[D]^d \quad \text{or} \quad R_b = K_b\,[C]^c\,[D]^d$$

Since chemical equilibrium is dynamic in nature representing the equal rate in both direction ($R_f = R_b$), therefore $K_f\,[A]^a\,[B]^b = K_b\,[C]^c\,[D]^d$

By rearranging this relation we get

$$\frac{K_f}{K_b} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

At any given temperature both K_f and Kb are constant, the ratio K_f/K_b will also be constant and collectively termed as equilibrium constant symbolized by K_c.

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

This is known as equilibrium expression or equilibrium law. It reveals that "when at a certain temperature a chemical reaction reaches to equilibrium state the ratio of active masses of products to reactants become constant".

2. State Le-Chatelier's principle. Explain the industrial application of Le-Chatelier's principle using Haber's process.

Ans)

Le-Chatelier's principle: It states that "If an external stress such as concentration, pressure or temperature is applied to a system at equilibrium, the equilibrium is disturbed and tends to shift in a direction to offset the effect of stress imposed".

Industrial application of le chatelier's principle (Haber's process): The synthesis of ammonia by Haber's process is an industrial application of Le-Chatelier's principle.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \; (\Delta H = \text{-ve})$$

1. Effect of Pressure: In the given equation four moles of gases on the left side and two mole on the right side, an increase in the pressure shifts the reaction on the right side and favours the formation of ammonia gas. Since a very high pressure may be dangerous for the process, an optimum pressure should be settled. The optimum compromising pressure to a good yield of ammonia is 200 to 300 atm.

2. Effect of Temperature: As the reaction is exothermic (ΔH^o = -ve), a decrease in temperature shift the reaction to the right side and favours the formation of NH_3 gas. The lowering in temperature do favours the high yield of ammonia but on the other hand it slows down the rate of reaction. The optimum choice of temperature on operational level is 400-500°C.

3. Effect of Concentration Change: Increase in concentration of nitrogen (N_2) or hydrogen (H_2) or decrease in the concentration of Ammonia (NH_3) shift the reaction in the forward direction and yield the maximum amount of ammonia.

4. Addition of Catalyst: Catalyst speed up the reaction without effecting on equilibrium position. Finely divided Iron is used as a catalyst in the synthesis of ammonia.

3. Give brief account on Common ion effect.

Ans)

Common ion effect:

Definition: To decrease the solubility of a sparingly soluble salt in solution by the addition of a highly soluble salt with one common ion refers as common ion effect.

Example: Consider the equilibrium settled when a saturated solution of silver chloride is prepared in water.

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

If now we add some amount of a soluble salt like sodium chloride (NaCl) which has Cl^- ion common to silver chloride. According to Le-Chatelier principle the increased Cl^- ions concentration in the solution produce a stress on AgCl equilibrium and to reduce this effect satisfactorily the excess Cl^- ions reacts with some Ag^+ ions and shift the equilibrium to the left and form precipitates of AgCl.

Application: Since common ion effect is related to the lowering in the solubility of slightly soluble salt in the precipitation formation, it plays versatile roles in many areas of analytical chemistry such as buffering of solutions, purification of salts, soap precipitation and other qualitative and quantitative analysis.

4. Define equilibrium constant (Kc). How it helps in predicting the

(i) Direction of reaction (ii) Extent of reaction.

Ans)

Equilibrium constant (Kc): For a chemical reaction, the equilibrium constant can be defined as the ratio between the amount of reactant and the amount of product which is used to determine chemical behaviour.

(i) Direction of reaction: Kc and reaction quotient are a very useful tool in determining whether the reaction has reached to equilibrium, if not, in which direction it proceed at that moment. The three possible cases are as follow.

Case-1: If Qc < Kc, indicates that the system proceeds from left to right to a greater extent and the rate of formation of product is higher. The reason is that the conc. of reactants (denominator) is large relative to the conc. of products (numerator) in the reaction quotient expression.

Case-2: If Qc > Kc, indicates that the system proceeds from right to left to a greater extent and the rate of formation of reactant is higher because the conc. of reactant (denominator) is smaller than conc. of product (numerator) in the reaction quotient expression.

Case-3: If Qc = Kc, indicates that the system is in dynamic equilibrium and the rate of reaction in both the directions remains same.

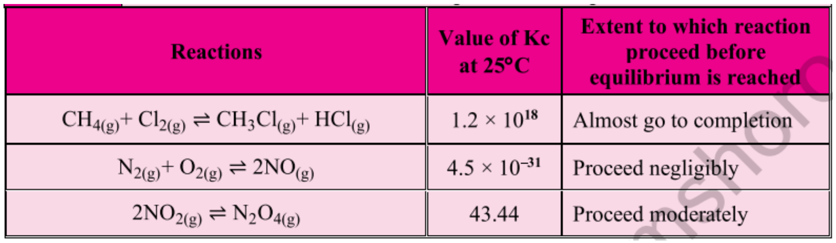
(ii) Extent of reaction: Since reactions have a long range of Kc values, the extent to which a chemical reaction proceeds is substantially discussed into three destinations in the reaction pathway.

Very large value of Kc shows that ratio of products to reactants at equilibrium is very large and it infers that reaction is nearly to completion.

Very small value of Kc shows that the ratio of products to reactants at equilibrium is very small and it infers that reaction proceeds hardly at all before reaching the equilibrium.

Intermediate value of Kc shows that appreciable amount of both reactants and products are present in the equilibrium mixture.

Prediction of extent of reaction at particular temperature:



Reactions	Value of Kc at 25°C	Extent to which reaction proceed before equilibrium is reached
$CH_{4(g)} + Cl_{2(g)} \rightleftharpoons CH_3Cl_{(g)} + HCl_{(g)}$	1.2×10^{18}	Almost go to completion
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	4.5×10^{-31}	Proceed negligibly
$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$	43.44	Proceed moderately

Numerical Questions

1. At 444°C reaction of hydrogen and iodine is performed in a sealed 1dm^3 steel vessel.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

If equilibrium mixture contains 1 mole of H_2, 1 mole of I_2 and 7 moles of HI. Calculate (a) Equilibrium constant (Kc) (b) Initial concentration of H_2 and I_2

Solution:

(a)

Since equilibrium moles of all components in the reacting mixture are given, we first convert them into molar concentration and then put into equilibrium expression to find out Kc.

$[H_2] = \frac{1}{1} = 1$ mol/dm^3

$[I_2] = \frac{1}{1} = 1$ mol/dm^3

$[HI] = \frac{7}{1} = 7$ mol/dm^3

Kc expression for the given reaction may be written as

$$Kc = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$Kc = \frac{(7)^2}{(1)(1)}$$

Kc = 49

(b)

	$H_{2\,(g)}$ +	$I_{2\,(g)}$ ⇋	$2HI_{(g)}$
Initial moles	x	x	0
Equilibrium moles	1	1	7

From this equation, we can see that for every mole of H_2 that reacts, one mole of I_2 is also consumed, and two moles of HI are formed.

So, at equilibrium, we have:

- Moles of H_2 utilized = x - 1
- Moles of I_2 utilized = x - 1
- Moles of HI formed = 2(x - 1) = 2x - 2

Now, we're given that at equilibrium, there are 7 moles of HI. Therefore, we can set up an equation:

$2x - 2 = 7$

x = initial conc. H_2 = initial conc. I_2 = 4.5 moles

2. Lead fluoride (PbF_2) is a high melting white solid used in glass coating to reflect IR rays. Its solubility in water at 25°C is 0.58g/dm³. Calculate its Ksp.

(A mass of Pb = 207 and F = 19)

Solution:

First write a net ionic equation of PbF_2, to note the number of coefficient of each ion. Then put the values of ionic concentration in Ksp expression:

$PbF_{2\,(s)} \leftrightharpoons Pb^{+2}_{(aq)} + 2F^{-}_{(aq)}$

Solubility in molar conc. = 0.00237 mol/dm^3

The ionic concentrations of 1 moles Pb^{+2} and 2 moles F^- are illustrated as

$[Pb^{+2}] = 1 \times 0.00237 = 0.00237$ mol/dm^3

$[F^-] = 2 \times 0.00237 = 0.00474$ mol/dm^3

Now inserting these values in ksp expression

$Ksp = [Pb^{+2}]\,[F^{-}]^{2}$

$Ksp = (0.00237)\,(0.00474)^{2} = 5.3 \times 10\text{-}8\ mol^{3}/dm^{9}$

3. A solution of $CaCO_3$ is prepared by mixing 200cm³ of 2.4×10^{-4} M $Ca(NO_3)_2$ and 300cm^3 of 4.5×10^{-2} M K_2CO_3. Will $CaCO_3$ precipitate upon cooling to 25°C if Ksp of $CaCO_3$ at 25°C is 3.8×10^{-9}.

Solution:

To solve this problem, first we determine the concentration of Ca^{+2} ions and CO_3^{-2} ion in the total volume of the mixture i.e. in 500 cm^3. Then determine ionic product (Qsp) and finally compare it with ksp value of $CaCO_3$, to decide whether precipitate will form or not

$[Ca^{+2}] = 2.4 \times 10^{-4}\ M \times \frac{200}{500} = 9.6 \times 10^{-5}\ M$

$[CO_3^{-2}] = 4.5 \times 10^{-2}\ M \times \frac{300}{500} = 0.027\ M$

Now substitute these ionic concentrations into ionic product expression

$Qsp = [Ca^{+2}]\,[CO_3^{-2}] = (9.6 \times 10^{-5})\,(0.027) = 2.592 \times 10^{-6}$

But Ksp of $CaCO_3$, is 3.8×10^{-9}

Because Qsp > ksp, precipitates of $CaCO_3$ will be formed in the solution.

4. In an equilibrium study of above reaction, 1.2 moles of H_2 and 1.2 moles of I_2 were injected in an evacuated 1000cm³ sealed flask and start the reaction to occur at 440°C until the equilibrium is formed. If Kc for this reaction is 49, calculate the equilibrium concentration of H_2, I_2 and HI.

Solution:

	$H_{2\,(g)}$	+ $I_{2\,(g)}$ ⇋	$2HI_{(g)}$
Initial moles	1.2	1.2	0
Equilibrium moles	1.2-x	1.2-x	2x
Equilibrium Conc.	(1.2-x)/1	(1.2-x)/1	2x/1

$$Kc = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$49 = \frac{(2x/1)^2}{((1.2-x)/1)((1.2-x)/1)}$$

$$49 = \frac{(2x)^2}{(1.2-x)^2}$$

$$49 = \frac{4x^2}{1.44 - 2.4x + x^2}$$

$$70.56 – 117.6\,x + 49\,x^2 = 4x^2$$

$$45x^2 – 117.6\,x + 70.56 = 0$$

$$x = 0.933 \text{ mol/dm}^3$$

At equilibrium;

$[H_2]$ = 1.2 - x = 1.2 – 0.933 = 0.267 mol/dm^3

$[I_2]$ = 1.2 - x = 1.2 – 0.933 = 0.267 mol/dm^3

[HI] = 2x = 2 x 0.933 = 1.866 mol/dm^3

Chapter 8: ACIDS, BASES AND SALTS

Multiple Choice Questions:

1. Choose the correct answer

(i) H_2SO_4 is stronger acid than CH_3COOH because:

(a) It gives two H ion per molecule
(b) Its boiling point is high
(c) Its degree of ionization is high
(d) It is highly corrosive

(ii) Al_2O_3 is amphoteric oxide because it reacts with:

(a) Acids
(b) Base
(c) Both acids and base
(d) neither acid nor base

(iii) Which of the following is not a Buffer solution:

(a) CH_3COOH/CH3COONa
(b) $Na_2CO_3/NaHCO_3$
(c) NH_4OH/NH_4Cl
(d) NaOH/HCl

(iv) Which oxide is amphoteric in nature:

(a) K_2O
(b) CO_2
(c) CaO
(a) Al_2O_3

(v) Which of the following does not alter the pH of a solution?

(a) NH_4Cl
(b) Na_2CO_3
(c) NaCl
(d) Mg(OH)Cl

(vi) Conjugated acid of NH_3 is:

(a)NH_4^+
(b) NH_2^-
(c) NH_2
(d) NH

(vii) Salt which is formed by the neutralization of weak acid and strong base is:

(a) $NaNO_3$
(b) NH_4Cl
(c) Na_2CO_3
(d) NH_4CN

(viii) Which of the following statements is not correct about the bases?

(a) They have bitter tastes (b) They have high pH value

(c)They react with acids to form salts (d) They turn blue litmus red

(ix) A conjugate acid base pair has the difference of only:

(a) One electron (b) One proton

(c) One electron pair (d) One proton pair

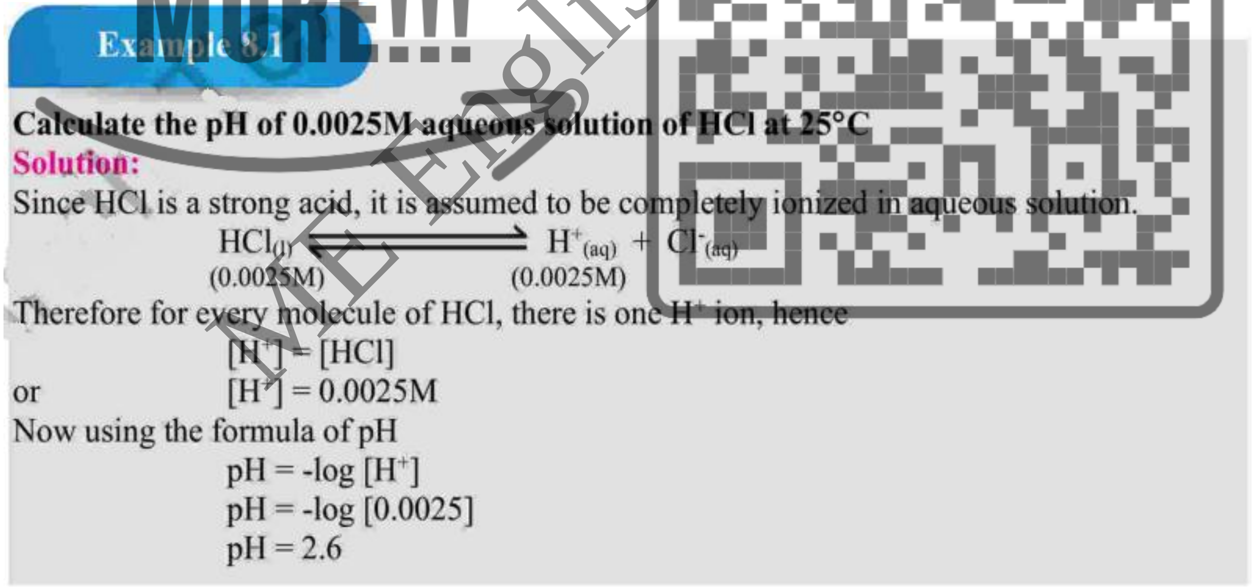
(x) Salt formed by neutralization of weak acid and weak base is:

(a) NH_4Cl (b) Na_2CO_3

(c) NH_4CN (d) Na_2SO_4

Key:

i. c	ii. c	iii. d	iv. d	v. c
vi. a	vii. c	viii. d	ix. b	x. c



Example 8.1

Calculate the pH of 0.0025M aqueous solution of HCl at 25°C

Solution:

Since HCl is a strong acid, it is assumed to be completely ionized in aqueous solution.

$$\underset{(0.0025M)}{HCl_{(l)}} \rightleftharpoons \underset{(0.0025M)}{H^+_{(aq)}} + Cl^-_{(aq)}$$

Therefore for every molecule of HCl, there is one H^+ ion, hence

$[H^+] = [HCl]$

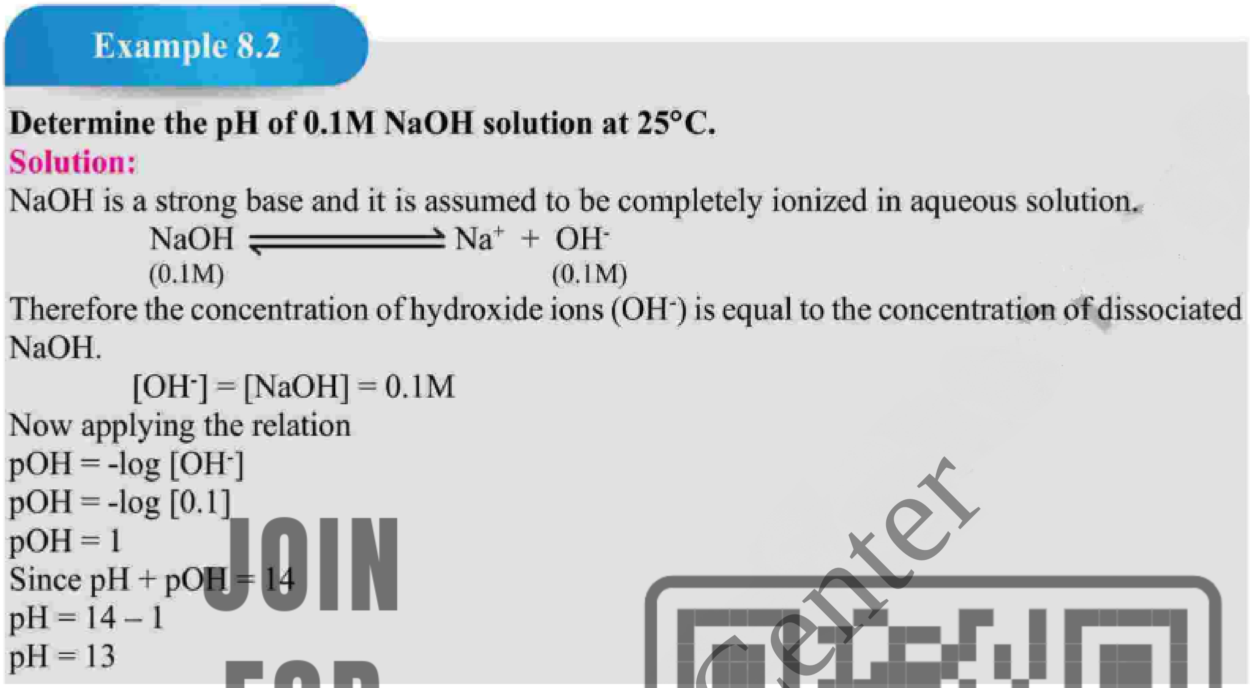
or $[H^+] = 0.0025M$

Now using the formula of pH

$pH = -\log [H^+]$

$pH = -\log [0.0025]$

$pH = 2.6$



Example 8.2

Determine the pH of 0.1M NaOH solution at 25°C.

Solution:

NaOH is a strong base and it is assumed to be completely ionized in aqueous solution.

$$\underset{(0.1M)}{NaOH} \rightleftharpoons Na^+ + \underset{(0.1M)}{OH^-}$$

Therefore the concentration of hydroxide ions (OH^-) is equal to the concentration of dissociated NaOH.

$$[OH^-] = [NaOH] = 0.1M$$

Now applying the relation

$pOH = -\log [OH^-]$

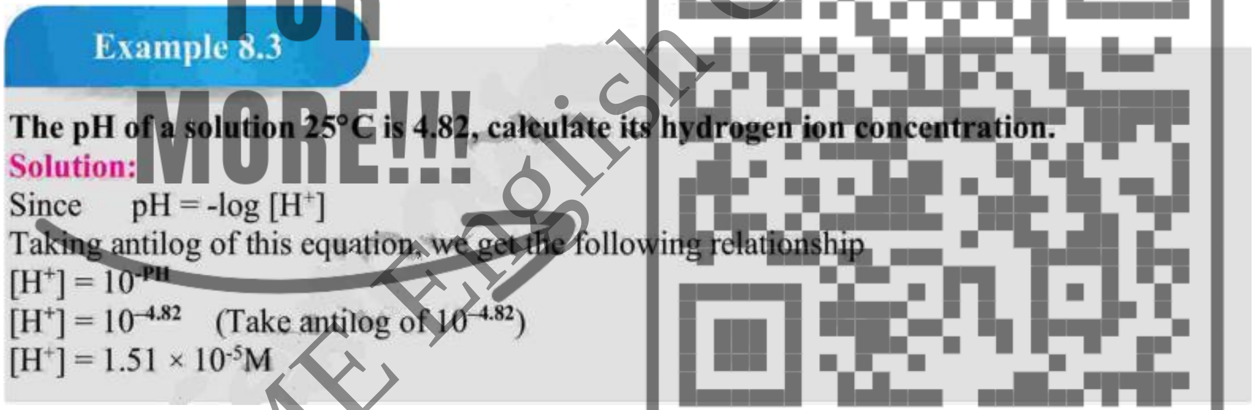
$pOH = -\log [0.1]$

$pOH = 1$

Since $pH + pOH = 14$

$pH = 14 - 1$

$pH = 13$



Example 8.3

The pH of a solution 25°C is 4.82, calculate its hydrogen ion concentration.

Solution:

Since $pH = -\log [H^+]$

Taking antilog of this equation, we get the following relationship

$[H^+] = 10^{-PH}$

$[H^+] = 10^{-4.82}$ (Take antilog of $10^{-4.82}$)

$[H^+] = 1.51 \times 10^{-5}M$

Short Questions

1. Define pH & pOH of a solution? Also show that pH+ pOH = 14.

Ans)

pH: pH i.e. power of hydrogen or hydronium ion is defined as “Log of reciprocal of hydrogen ion or hydronium ion concentration or negative log of hydrogen or hydronium ion concentration”.

pOH: pOH i.e. power of hydroxyl ion is defined as "Log of reciprocal of hydroxyl ion concentration or negative log of hydroxyl ion concentration".

Prove of pH+ pOH = 14:

As we known

$K_w = [H3O^+]\ [OH^-]$ or $[H^+]\ [OH^-] = 1 \times 10^{-14}$

Or

$[H3O^+]\ [OH^-]$ or $[H^+]\ [OH^-] = 10^{-14}$

Taking log of both sides

$\log [H3O^+]\ [OH^-]$ or $\log [H^+]\ [OH^-] = \log 10^{-14}$

Using log properties

$\log [H3O^+] + \log [OH^-]$ or $\log [H^+] + \log [OH^-] = -14 \log 10$

$\log [H3O^+] + \log [OH^-]$ or $\log [H^+] + \log [OH^-] = -14 \times 1$

Multiplying both sides by negative

$-\log [H3O^+] - \log [OH^-]$ or $-\log [H^+] - \log [OH^-] = 14$

Or

$\{-\log [H3O^+]\} - \log \{[OH^-]\}$ or $\{-\log [H^+]\} + \{-\log [OH^-]\} = 14$

As $-\log [H_3O^+]$ or $-\log [H^+]$ is pH and $-\log [OH^-]$ is pOH

so above expression becomes

pH + pOH = 14

2. Why the aqueous solution of NH_4Cl is acidic and Na_2CO_3 is alkaline.

Ans) The aqueous solution of NH_4Cl is acidic because it produces hydronium ions (H_3O^+) when it dissolves in water, while the solution of Na_2CO^3 is alkaline because it generates hydroxide ions (OH^-). This is due to the acid-like and base-like properties of their respective ions when they interact with water.

3. Write down conjugate base of each of the following acids.

H_2SO_4, H_2S, NH_4^+, HCOOH

Ans)

Acid	Conjugate base
H_2SO_4	HSO^{4-}
H_2S	HS^-
NH_4^+	NH_3
HCOOH	$HCOO^-$

4. What is meant by self-ionization of water? Write the expression of Kw. What is its value at 25°C?

Ans) Self-ionization of water: The reaction in which a water molecule donates one of its protons to a neighbouring water molecule, either in pure water or in an aqueous solution, is called the self-ionization of water.

Ionization Constant of Water (Kw): Although water is chemically non electrolytic substance, however it conducts electricity to a very small extent due to its self-ionization ability. During the reaction proton from one water molecule is transferred to another water molecule as given in the following reaction.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The equilibrium constant may be written as

$$K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

$K[H_2O]^2 = [H_3O^+][OH^-]$ (Hence concentration of water is constant)

$Kw = [H_3O^+][OH^-]$

Value of Kw at 25 ^oC: At 25°C, the value of Kw is 1.0×10^{-14}.

5. Write equation and indicate the conjugate acid-base pairs for the following:

(i) Acetic acid & ammonia **(ii) Hydrochloric acid & water**

Ans)

(i) $CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$

Conjugate acid: NH_4^+

Conjugate base: CH_3COO^-

(ii) $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

Conjugate acid: H_3O^+

Conjugate base: Cl^-

Descriptive Questions

1. Explain Bronsted-Lowry theory of acids and bases. What is meant by conjugate acid- base pair give examples?

Ans)

The Bronsted-Lowry Theory of acids and bases:

Definition: According to this theory "Acid is a species which tends to donate proton (protogenic) whereas base is a species that accept proton (protophillic). Further, an acid base reaction is the transfer of proton from acid to base".

Example#1: Let us consider what happens when a strong acid (HCl) dissolves in water and undergo ionization.

$$\underset{\text{(acid)}}{HCl_{(l)}} + \underset{\text{(base)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(conjugate acid)}}{H_3O^+_{(aq)}} + \underset{\text{(conjugate base)}}{Cl^-_{(aq)}}$$

Since HCI donate a proton, it acts as an acid on the other hand water (H2O) accept a proton and serve as base.

Look at the reverse of this acid base reaction where hydroxonium ion (H_3O^+) react with chloride ion (CI-). In the reverse reaction, H_3O^+ act as conjugate acid while Cl^- ion serves as conjugate base. Thus the equilibrium of the above reaction represents two acids and two bases, one on either side of the reaction arrow.

Example#2: Now see the ionization of ammonia in to water in the given equilibrium.

$$\underset{\text{(base)}}{NH_{3(g)}} + \underset{\text{(acid)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(conjugate acid)}}{NH^+_{4(aq)}} + \underset{\text{(conjugate base)}}{OH^-_{(aq)}}$$

Reaction in the forward direction shows that water gives up a proton (acid) and ammonia accept it (base). In reverse phase of this reaction ammonium ion ($NH_4{}^+$) acts as conjugate acid and hydroxide ion (OH^-) as conjugate base.

While studying above two acid base reactions it is interesting to note that water serves as base when HCl is dissolved into it but acts as acid when ammonia is added.

Conjugate acid base pairs: A conjugate acid base pair represents two species, one on the left side and other on the right side of equation with the difference of one proton.

Consider the reaction of H_2S and NH_3.

$$H_2S_{(g)} + NH_{3(aq)} \rightleftharpoons HS^-_{(aq)} + NH^+_{4(aq)}$$

To identify a conjugate acid base pair, it should be in our mind that the only difference between the two species is a proton (H^+). Here we see that H_2S change into HS^- by losing a proton. Thus H_2S and HS^- represents a conjugate acid base pair. NH_3 on the other hand accept a proton and change into $NH_4{}^+$ therefore it is another conjugate acid base pair.

$$\underset{\text{(Bronsted acid)}}{H_2S} + \underset{\text{(Bronsted base)}}{NH_3} \rightleftharpoons \underset{\text{(Conjugate acid)}}{NH_4^+} + \underset{\text{(Conjugate base)}}{HS^-}$$

Bronsted Acid		Bronsted Base		Conjugate Acid		Conjugate Base
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
CH_3COOH	+	NH_3	$\rightleftharpoons$	NH_4^+	+	CH_3COO^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
HBr	+	F^-	$\rightleftharpoons$	HF	+	Br^-
H_2O	+	CO_3^{-2}	$\rightleftharpoons$	HCO_3^-	+	$O\bar{H}$
HSO_4^-	+	CO_3^{-2}	$\rightleftharpoons$	HCO_3^-	+	SO_4^{-2}

2. Define the process of hydrolysis. Explain the behavior of each of the following salts in aqueous solution. (i) K_2CO_3 (ii) $(NH_4)_2SO_4$ (iii) $NaNO_3$

Ans)

Hydrolysis: The reaction of cation or anion of the salt with water to produce hydrogen ions (H^+) or hydroxyl ions (OH^-) and change the pH of solution is known as hydrolysis.

(i) Behavior of K_2CO_3: It is the salt of weak acid and strong base. The cat ion which comes from strong base does not react further with water. The anion which comes from weak acid reacts with water and undergoes hydrolysis to give alkaline solution having pH more than 7.

$$K_2CO_{3(s)} \rightleftharpoons 2K^+_{(aq)} + CO_3^{-2}$$

$$CO_3^{-2} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$$

(ii) Behavior of $(NH_4)_2SO_4$: It is the salt of strong acid and weak base. The anion of these salts comes from strong acid and hence does not react with water, however cat ion which comes from weak base interact with water to give acid solution having pH less than 7.

$$(NH_4)_2SO_4(s) \rightleftharpoons 2NH_4^+ + SO_4^{-2}{}_{(aq)}$$

$$2NH_4^+ + 2H_2O \rightleftharpoons 2NH_3 + 2H_3O^+$$

(iii) Behavior of $NaNO_3$: It is the salt of strong acid and strong base. Since both cation and anion comes from strong base and strong acid respectively, they do not undergo hydrolysis and hence the pH of their aqueous solution remains 7.

$$NaNO_{3(s)} \rightleftharpoons Na^+_{(aq)} + NO_3^-{}_{(aq)}$$

3. What is Buffer solution? Explain how it resists the change of pH by adding small amount of acid and base. Give the applications of buffer solution.

Ans)

Buffer solution: Buffer solution is a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid. It resists the change in pH and can keep it for long time.

Buffer Action: To understand how a buffer works, let us consider the ionization of acetic acid-sodium acetate solution.

$$CH_3COOH_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
$$CH_3COONa_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

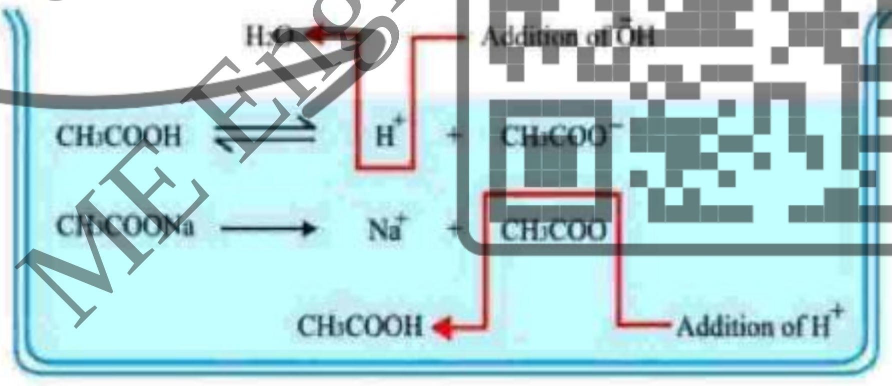
Both acetic acid and sodium acetate provides CH3COO$^-$ ions, however CH_3COO^- ions comes from CH_3COONa (strong basic salt) are in high concentration.

When small amount of an acid is added to this buffer solution, the most of the H+ ions of acid combine with excess acetate ions (CH3COO-) of the solution to form acetic acid.

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(l)}$$

Thus a very slightly change in the PH is observed and we say that pH remains practically unchanged.

When small amount of a base in added to this buffer solution the additional OH^- ions combine with H^+ ions of the buffer to form water molecules. As a result the equilibrium shifts to the right to produce more H^+ ions till practically all the excess of OH^- ions are neutralized and the original buffer pH is restored.



Buffer action of an acidic buffer

Application of Buffer solutions:

1. Buffer solution plays a very significant role in biochemical system. For example pH of our blood is maintained at 7.3 to 7.4 due to bicarbonate and carbonic acid buffer.

2. Buffer solutions are widely used in industrial processes such as fermentation, dye processes and manufacturing of pharmaceuticals.
3. Buffer solution is used in agriculture to maintain the pH of soil for proper crop yield.
4. Buffer solution is extensively used in analytical chemistry and pathological laboratories.
5. Buffers are also used in foods industries to maintain the pH of various food items in order to preserve their flavor, appearance and micro-biological stability.

4. Describe Lewis theory of acids and bases. What are the advantages of this theory over Lowry Bronsted theory?

Ans)

Lewis definition of acids and bases: According to GN Lewis (1923) "Acid is a substance that accepts an electron pair whereas base is a substance that can donates electron pair".

Example#1: Considering Lewis concept, hydrogen ion (H^+) is an acid because it accepts electron pair. Similarly hydroxide ion (OH^-) is base since it donate lone pair of electron.

Example#2: Several neutral molecules such as $AlCl_3$, BF_3, $FeCl_3$ etc serves as Lewis acids due to electron deficiency on the central atom (fewer than eight valence electrons). On the other hand ammonia (NH_3), Phosphene (PH_3), Water (H_2O) etc although have their complete octet but possess lone pair of electron that is available to donate hence they serves as Lewis base.

Advantages:

1. **Broader Applicability:** Lewis theory covers a wider range of reactions, including non-aqueous systems and covalent compounds.
2. **Electron Pair Perspective:** It defines acids as electron pair acceptors and bases as electron pair donors, providing a fundamental understanding of electron transfer.

3. **Coordination Chemistry:** Explains the formation of coordination complexes, where metal ions act as Lewis acids.
4. **Predicting Geometry:** Helps predict molecular and complex ion geometries based on electron pairs.
5. **Organometallic Chemistry:** Essential in organometallic chemistry for understanding metal-ligand interactions.

5. What is salt? Explain Acidic, Basic and Neutral salts?

Ans)

Salts: Salt is a substance produced by the reaction of acid and base. It consists of positive ion of base and negative ion of acid.

Neutral salts: These salts are formed by neutralization of strong acid and strong base. Since both cation and anion comes from strong base and strong acid respectively, they do not undergo hydrolysis and hence the pH of their aqueous solution remains 7.

Example: NaCl, K_2SO_4, $NaNO_3$ etc.

Acidic salts: These salts are formed by neutralization of strong acid and weak base. The anion of these salts comes from strong acid and hence does not react with water, however cat ion which comes from weak base interact with water to give acid solution having pH less than 7.

Example: When NH_4Cl dissolves in water, it gives acidic solution.

$$NH_4Cl_{(s)} \rightleftharpoons NH_4^+ + Cl^-_{(aq)}$$

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

Other examples of this type of salts are $(NH_4)_2SO_4$, $CuCl_2$ etc.

Basic salts: These salts are formed by neutralization of weak acid and strong base. The cat ion which comes from strong base does not react further with water. The anion which comes from weak acid reacts with water and undergoes hydrolysis to give alkaline solution having pH more than 7.

Example: Sodium carbonate when dissolved in water it gives basic solution.

$$Na_2CO_{3(s)} \rightleftharpoons 2Na^+_{(aq)} + CO^{-2}_{3\,(aq)}$$
$$CO_3^{-2} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$$

Other examples of this type of salt are CH_3COONa, $NaHCO_3$ etc.

Numerical Questions

1. A solution is made by dissolving 14.8g HCl in water at 25°C. If the volume of solution is 750 cm^3 and HCl is assumed to be completely ionized, calculate its pH.

Data:

m = 14.8g

V = 750 cm^3 = 750/1000 = 0.75 dm^3

pH = ?

Solution:

$n = \frac{m}{M} = \frac{14.8}{36.5} = 0.405$ moles

Molarity = $\frac{n}{V} = \frac{0.405}{0.75} = 0.54$ M

$HCl \rightleftharpoons H^+ + Cl^-$

0.54 M 0.54 M

$[H^+]$ = 0.54 M

pH = -log $[H^+]$

pH = -log(0.54)

pH = 0.267

2. The hydroxide ion concentration in an antiseptic solution at 25°C is 3.5×10^{-4} M. Calculate its pH.

Data:

$[OH^-] = 3.5 \times 10^{-4}$ M

pH = ?

Solution:

$pOH = -\log [H^+]$

$pOH = -\text{Log}(3.5 \times 10^{-4})$

pOH = 3.46

pH + pOH = 14

pH + 3.46 = 14

pH = 10.54

Chapter 9: CHEMICAL KINETICS

Multiple Choice Questions

Choose the correct answer:

(1) For a hypothetical reaction $x+y \longrightarrow z$, if the conc. of x is double, the rate increases by square and if the cone, of y is doubled the rate increases by twice. The experimental rate law of this reaction is:

(a) $R = K [x]^1 [y]^1$

(b) $R = K [x]^1[y]^2$

(c) $R = K [x]^2 [y]^1$

(d) $R = K [x]^2 [y]^2$

(ii) The unit of rate constant (K) for the first order reaction is:

(a) s^{-1}

(b) conc. s^{-1}

(c) conc.$^{-1}$ s

(d) conc.$^{-1}$ s^{-1}

(iii) Rate constant of a reaction is affected by:

(a)Conc. of reactants

(b) Conc. of products

(c) Temperature

(d) Reaction time

(iv) The purpose of using of catalyst in a chemical reaction is to change:

(a) Equilibrium constant

(b) Enthalpy of reaction

(c) Activation energy

(d) Nature of reaction

(v) The overall order of reaction to which the rate law is R=K:

(a) Zero order

(b) First order

(c) Second order

(d) Third order

(vi) Ionic reactions are classified into:

(a) Slow reaction

(b) Moderate reactions

(c) Fast reactions

(d) Reversible reaction

(vii) The decomposition of H_2O_2 is inhibited by:

(a) 2% ethanol

(b) Glycerin

(c) MnO_2 (d) V_2O_5

(viii) The best alternative term for the velocity of reaction is:

(a) Rate of appearance (b) Rate of disappearance

(c) Average rate (d) Instantaneous rate

(ix) Order of reaction is the power to which concentration of reactant is:

(a) Lowered (b) Raised

(c) Stopped (d) Constant

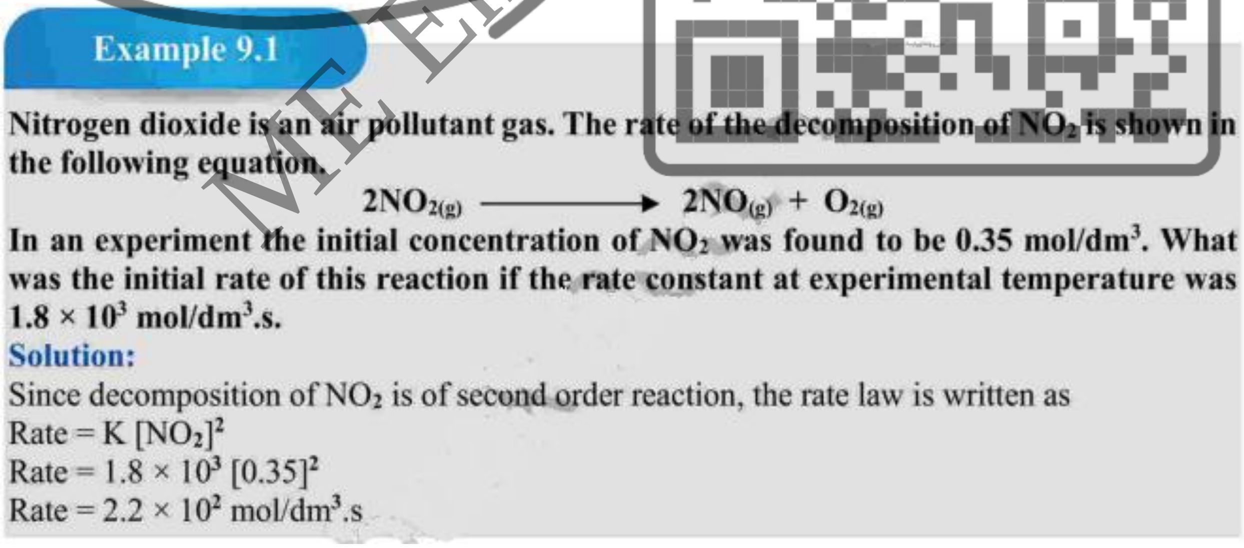
(x) In the reaction A→B, the rate of disappearance is written as:

(a) $\frac{dA}{dt}$ (b) $\frac{-dA}{dt}$

(c) $\frac{dB}{dt}$ (d) $\frac{-dB}{dt}$

KEY:

i. c	ii. a	iii. c	iv. c	v. a
vi. c	vii. b	viii. d	ix. b	x. b



Example 9.1

Nitrogen dioxide is an air pollutant gas. The rate of the decomposition of NO_2 is shown in the following equation.

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

In an experiment the initial concentration of NO_2 was found to be 0.35 mol/dm³. What was the initial rate of this reaction if the rate constant at experimental temperature was 1.8×10^3 mol/dm³.s.

Solution:

Since decomposition of NO_2 is of second order reaction, the rate law is written as

$\text{Rate} = K[NO_2]^2$

$\text{Rate} = 1.8 \times 10^3 [0.35]^2$

$\text{Rate} = 2.2 \times 10^2$ mol/dm³.s

Example 9.2

The initial rate data obtained in a series of experiments while working on the oxidation of nitric oxide to give nitrogen dioxide is given in the following table. Determine its rate law and find the order of reaction.

$$NO + O_2 \longrightarrow NO_2$$

Experiment No.	Initial [NO]	Initial $[O_2]$	Initial Rate
1	0.10M	0.10M	8×10^{-4} Ms^{-1}
2	0.10M	0.20M	16×10^{-4} Ms^{-1}
3	0.20M	0.10M	16×10^{-4} Ms^{-1}

Solution:

(i) When the initial concentration of NO is doubled (experiment 1 and 3), the initial rate is also doubled. Thus rate law with respect to A is.

$$R \propto [A]^1$$

(ii) When the initial concentration of O_2 is doubled (experiment 1 and 2), the initial rate is also doubled. Thus rate law with respect to B is.

$$R \propto [B]^1$$

(iii) The overall rate law now written as

$$R = K\,[A]^1\,[B]^1$$

(iv) Order of reaction is thus 1 + 1 = 2

Example 9.3

Decomposition of SO_2Cl_2 is of first order reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ write its rate law and deduce the unit of rate constant.

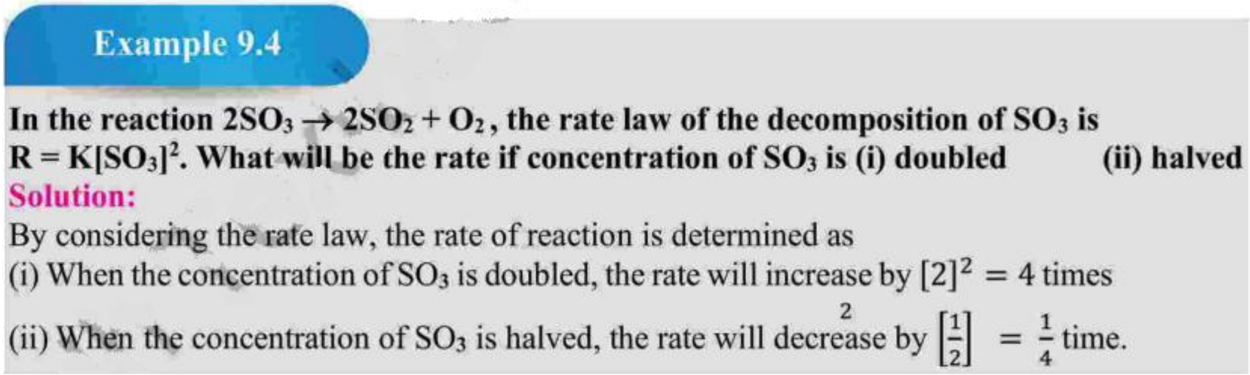
Solution:

Since decomposition of SO_2Cl_2 is governed by first order kinetics the rate law is written as Rate = K $[SO_2Cl_2]$

Now the unit of rate constant (K) is obtained if we put the units of concentration and unit of rate of reaction in the rate law.

$$K = \frac{mol/dm^3.s}{mol/dm^3}$$

$$K = s^{-1}$$



Example 9.4

In the reaction $2SO_3 \rightarrow 2SO_2 + O_2$, the rate law of the decomposition of SO_3 is $R = K[SO_3]^2$. What will be the rate if concentration of SO_3 is (i) doubled (ii) halved

Solution:

By considering the rate law, the rate of reaction is determined as

(i) When the concentration of SO_3 is doubled, the rate will increase by $[2]^2 = 4$ times

(ii) When the concentration of SO_3 is halved, the rate will decrease by $\left[\frac{1}{2}\right]^2 = \frac{1}{4}$ time.

Short Questions

1. Define the following:

(a) Rate of reaction (b) Velocity of reaction

(c) Order of reaction (d) Rate constant

Ans)

(a) **Rate of reaction:** Increase in the molar concentration of products or decrease in the molar concentration of reactants per unit time.

(b) Velocity of reaction: Velocity of reaction or rate of reaction is the increase in the molar concentration of products or decrease in the molar concentration of reactants per unit time.

(c) Order of reaction: The sum of all the exponents of the concentration in terms of reactants involve in the rate law is called order of reaction.

(d) Rate constant: It is a proportionality constant that relates the reaction rate to the concentrations of the reactants in a chemical reaction.

2. The rate law of the reaction $2NO + Br_2 \rightarrow 2NOBr$ is given as Rate= $K [NO]^2[Br_2]$, What is the order of reaction?

(i) With respect to each reactant. (ii) Overall reaction.

Ans)

The reaction $2NO + Br_2 \rightarrow 2NOBr$ follows the mechanism:

(1) $NO + Br2 \rightleftharpoons NOBr_2$ (Fast)
(2) $NOBr_2 + NO \rightarrow 2NOBr$ (Slow)

The rate expression is derived by step II of the mechanism, as it is the slower one

rate = $k [NOBr_2] [NO]$ ……….(i)

However, $NOBr_2$ is an intermediate and thus its concentration should be replaced from equation (i)

From step (1),

Equilibrium constant, $K_c = \frac{[NOBr_2]}{[NO]_2[Br_2]}$

$[NOBr_2] = Kc\ [NO]\ [Br_2]$ ……….(ii)

Then by equation (i) and (ii)

rate = $k'\ [NO]^2\ [Br_2]$

Overall order of the reaction = 1+2 = 3

3. How can you define order of reaction? What are the units for the rate constants of zero order, first order and second order reactions?

Ans)

Order of reaction: The sum of all the exponents of the concentration in terms of reactants involve in the rate law is called order of reaction.

Order of reaction	**Unit of rate constant**
Zero order	M/s
First order	1/s
Second order	1/(M.s)

4. Explains the following

(i) Powdered marble ($CaCO_3$) reacts quickly with hydrochloric acid than solid lump of marble.

(ii) Milk sour more rapidly in summer than in winter.

(iii) Reactants in solution reacts faster at high concentration.

(iv) Raising the temperature causes an increase in the rate of reaction.

Ans)

(i) Powdered marble ($CaCO_3$) reacts more quickly with hydrochloric acid (HCl) than a solid lump of marble due to the significantly larger surface area of the powdered form. The increased surface area allows for more frequent and effective collisions between $CaCO_3$ particles and HCl molecules, resulting in a faster reaction rate. In contrast, a solid lump of marble has a limited surface area exposed to the acid, leading to fewer collision opportunities and a slower reaction rate.

(ii) Milk sours more quickly in the summer compared to winter due to higher temperatures in summer. Warm temperatures encourage the rapid growth of bacteria and lactic acid-producing microorganisms in milk, leading to faster souring.

(iii) In a solution, reactants tend to react faster when their concentration is high. This is because higher concentrations result in more frequent collisions between reactant particles, increasing the chances of effective collisions that lead to the reaction. The greater the concentration, the faster the reaction rate, as described by the rate law for the specific reaction.

(iv) Raising the temperature increases the rate of a chemical reaction because it boosts the kinetic energy of molecules. This higher energy makes molecules collide more frequently and with greater force, increasing the chances of successful reactions.

5. Differentiate between the following

(i) Rate of reaction and rate constant (ii) Homogenous and Heterogeneous catalyst

(iii) Positive catalyst and inhibitor (iv) Elementary and overall reaction

Ans)

(i)

Rate of Reaction	Rate Constant
The rate at which a chemical reaction proceeds over time, typically expressed as the change in concentration of reactants or products per unit of time.	A constant specific to a particular chemical reaction at a given temperature that appears in the rate equation.
Expressed in units like moles per liter per second (mol/L·s) or molarity per second (M/s).	Units depend on the overall reaction order and can vary.
Can change as the reaction progresses and reactant concentrations change.	Remains constant at a given temperature for a specific reaction.
Determined experimentally by measuring changes in reactant or product concentrations over time.	Determined experimentally by measuring reaction rates at different concentrations and temperatures.

(ii)

Homogeneous Catalyst	Heterogeneous Catalyst
In a homogeneous catalyst, the catalyst exists in the same phase (usually liquid or gas) as the reactants.	In a heterogeneous catalyst, the catalyst exists in a different phase (usually solid) from the reactants.
Catalyst molecules are in direct contact with the reactant molecules throughout the reaction.	Reactants are adsorbed onto the surface of the catalyst, where the reaction occurs at the catalyst's active sites.
Typically difficult to separate the catalyst from the	Easier to separate the solid catalyst from the

reaction products due to being in the same phase.	reaction products, making catalyst recovery more straightforward.
Examples include homogeneous acid catalysis (e.g., H2SO4 in esterification) and homogeneous transition metal complex catalysis (e.g., Wilkinson's catalyst).	Examples include catalytic converters in cars (Pt, Pd, or Rh metals), catalysts used in industrial processes (e.g., iron in Haber-Bosch process), and enzymes in biological systems.

(iii)

Positive Catalyst (Catalyst)	**Inhibitor**
Increases the rate of a chemical reaction.	Decreases the rate of a chemical reaction.
Facilitates the reaction by providing an alternative reaction pathway with lower activation energy.	Hinders the reaction by interfering with the reaction mechanism or reducing the effective concentration of reactants.
Present throughout the reaction and actively participates in reaction steps.	Present throughout the reaction but does not actively participate in reaction steps; it exerts its effect by its presence.
Increases the rate constant (k) in the rate equation.	Decreases the rate constant (k) in the rate equation.

(iv)

Elementary Reaction	**Overall Reaction**
A single, individual step in a complex reaction mechanism, representing the collision and transformation of reactant molecules into products.	The overall chemical equation that summarizes the entire reaction, often consisting of multiple elementary reactions.
Follows a specific rate law equation, which can be determined experimentally for that specific step.	The rate law for the overall reaction is usually derived from the slowest (rate-determining) elementary step.
The reaction order with respect to each reactant can differ from one elementary reaction to another within the same reaction mechanism.	The reaction order is determined by the coefficients in the overall chemical equation and is constant for the entire reaction.
Can be unimolecular (involving a single molecule), bimolecular (involving two molecules), or termolecular (involving three molecules), depending on the collision of reactants.	Typically does not specify the molecularity of the reaction, as it represents the net result of multiple elementary reactions.

Chapter 10: SOLUTION AND COLLOIDS

Multiple Choice Questions

1. Choose the correct answer

(i) Only one pair of liquid in the following set does not obey Roault law, identify it:

(a) Methanol and Ethanol (b) Benzene and toluene

(c) n-Hexane and n-heptane (d) Ethanol and Acetone

(ii) Identify the incorrect statement about colloidal solution:

(a) It shows Tyndall effect (b) Its particles movement is Brownian type

(c) Its particle size is less than 1 nm (d) Its physical appearance is translucent

(iii) Effect of pressure change play significant role in the solubility of:

(a) Solid into liquid (b) Liquid into liquid

(c) Gas into liquid (d) All of them

(iv) Which is not a colligative property:

(a) Lowering in vapours pressure (b) Elevation in boiling point

(c) Depression in freezing point (d) Atmospheric pressure

(v) According to Raoult law the relative lowering of vapour pressure is equal to:

(a) Mole fraction of solvent (b) Mole fraction of solute

(c) Molality (d) Molarity

(vi) The sum of mole fractions of components of a solution is equal to:

(a) 0.0 (b) 1.0

(c) 10 (d) 100

(vii) How many moles of NaOH are present in a 2dm³ of 1 molar aqueous solution of it.

(a) 0.5 mole (b) 1 mole

(c) 1.5 mole (d) 2 mole

(viii) A colloidal solution of liquid into liquid is known as:

(a) Gel (b) Foam

(c) Sol (d) Emulsion

(ix) An example of completely immiscible liquid pair is:

(a) Benzene to toluene (b) Water and phenol

(c) Water and Benzene (c) Water and Benzene

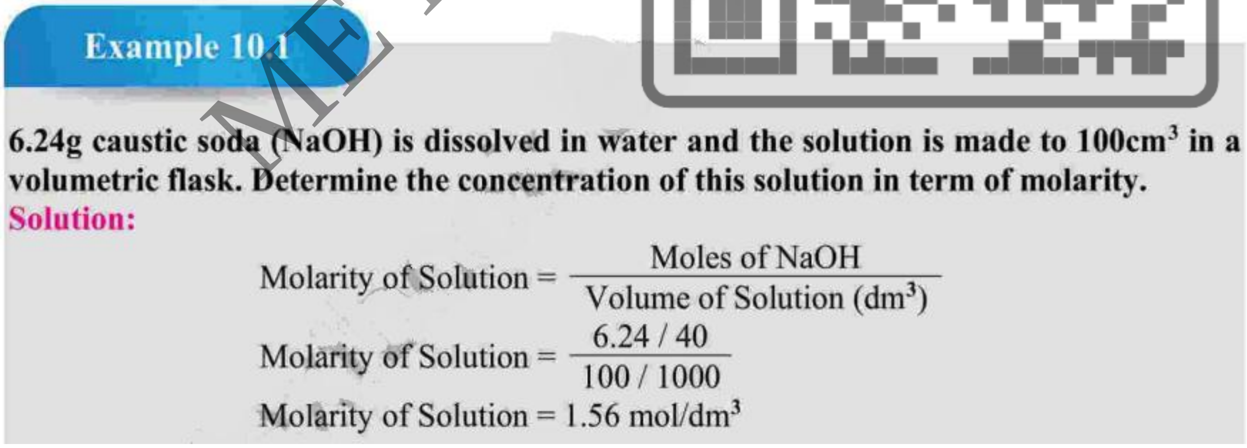
(x) A 15% W/W KOH solution can be prepared by mixing 15g KOH in:

(a) 15g water (b) 85g water

(c) 100g water (d) 115g water

KEY:

(i) d	(ii) c	(iii) c	(iv) d	(v) b
(vi) b	(vii) d	(viii) d	(ix) c	(x) b



Example 10.1

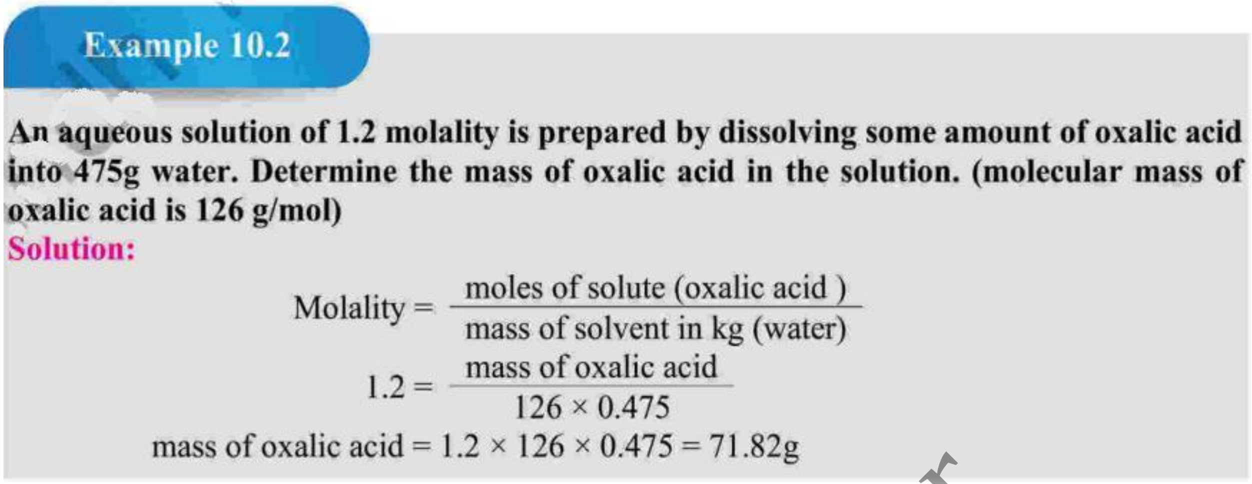
6.24g caustic soda (NaOH) is dissolved in water and the solution is made to 100cm³ in a volumetric flask. Determine the concentration of this solution in term of molarity.

Solution:

$$\text{Molarity of Solution} = \frac{\text{Moles of NaOH}}{\text{Volume of Solution (dm}^3)}$$

$$\text{Molarity of Solution} = \frac{6.24 / 40}{100 / 1000}$$

$$\text{Molarity of Solution} = 1.56\ \text{mol/dm}^3$$



Example 10.2

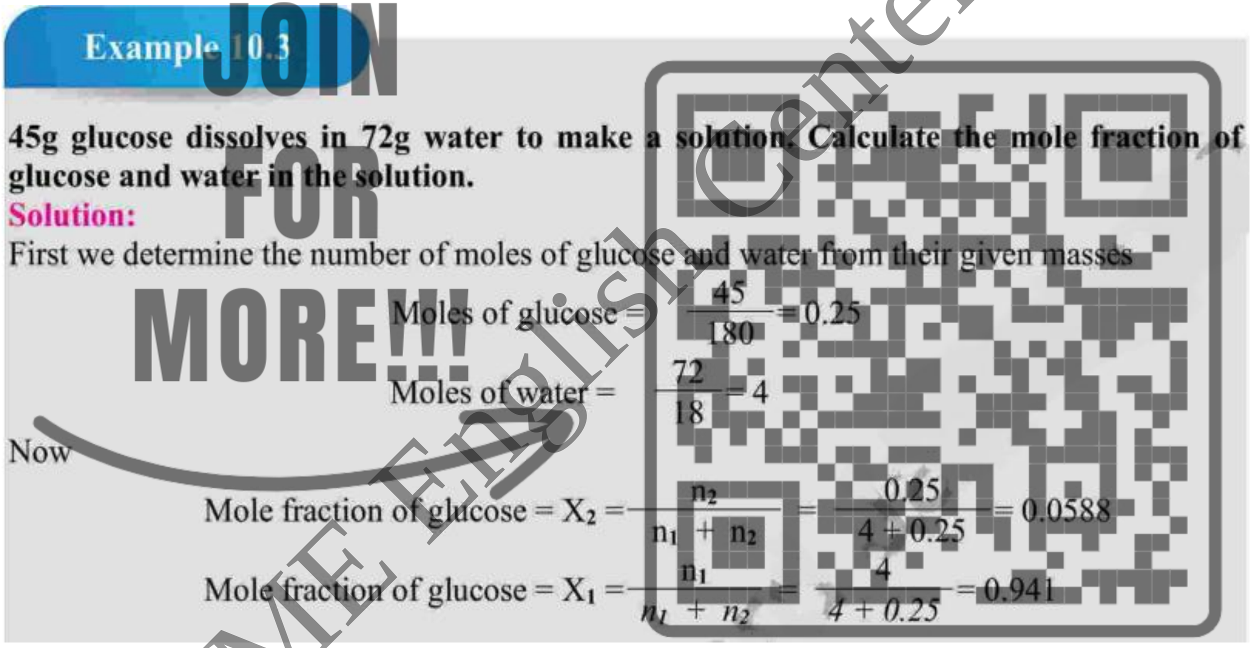
An aqueous solution of 1.2 molality is prepared by dissolving some amount of oxalic acid into 475g water. Determine the mass of oxalic acid in the solution. (molecular mass of oxalic acid is 126 g/mol)

Solution:

$$\text{Molality} = \frac{\text{moles of solute (oxalic acid)}}{\text{mass of solvent in kg (water)}}$$

$$1.2 = \frac{\text{mass of oxalic acid}}{126 \times 0.475}$$

$$\text{mass of oxalic acid} = 1.2 \times 126 \times 0.475 = 71.82\text{g}$$



Example 10.3

45g glucose dissolves in 72g water to make a solution. Calculate the mole fraction of glucose and water in the solution.

Solution:

First we determine the number of moles of glucose and water from their given masses

$$\text{Moles of glucose} = \frac{45}{180} = 0.25$$

$$\text{Moles of water} = \frac{72}{18} = 4$$

Now

$$\text{Mole fraction of glucose} = X_2 = \frac{n_2}{n_1 + n_2} = \frac{0.25}{4 + 0.25} = 0.0588$$

$$\text{Mole fraction of glucose} = X_1 = \frac{n_1}{n_1 + n_2} = \frac{4}{4 + 0.25} = 0.941$$

Example 10.4

Calculate the molality of a 12% urea solution (molar mass of urea is 60g/mol)

Solution:

(i) 12% urea solution represents 12g urea in 100g solution thus the mass of water is calculated as

Mass of water in gram = 100 – 12 = 88g

Mass of water in kg $= \frac{88}{1000} = 0.088$kg

(ii) No. of moles of urea $= \frac{\text{mass of urea}}{\text{molar mass of urea}}$

No. of moles of urea $= \frac{12}{60} = 0.2$ moles

(iii) Molality of urea $= \frac{\text{moles of urea}}{\text{mass of water (kg)}}$

Molality of urea $= \frac{0.2}{0.088} = 2.27$ mol/kg

Example 10.5

In the analysis of water sample, it was reported that 1g of water contains 6.34×10^{-3} mg magnesium ions. Calculate the concentration of magnesium ions in ppm.

Solution:

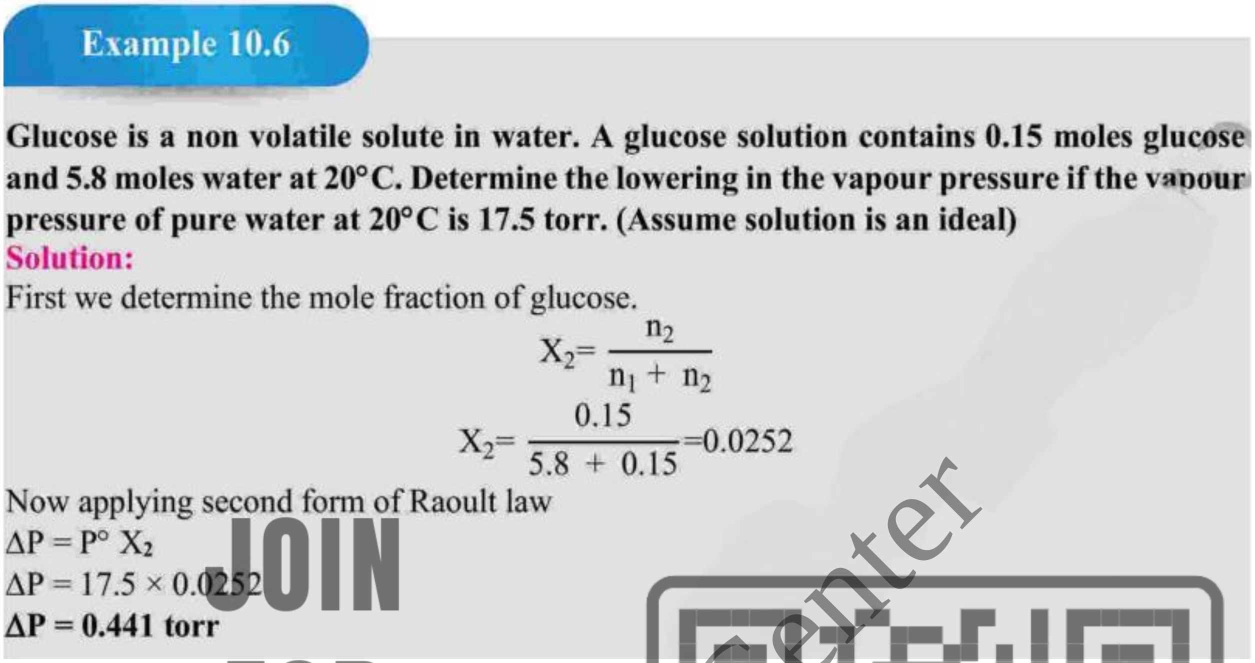
We know that

$$\text{ppm} = \frac{\text{amount of solute}}{\text{amount of solvent}} \times 10^6$$

$$\text{ppm} = \frac{6.34 \times 10^{-3}\,\text{mg}}{1\text{g}} \times 10^6$$

$$\text{ppm} = \frac{6.34 \times 10^{-3}\,\text{mg}}{10^3\,\text{mg}} \times 10^6 = 6.34$$

Thus concentration of magnesium ions in water = 6.34ppm



Example 10.6

Glucose is a non volatile solute in water. A glucose solution contains 0.15 moles glucose and 5.8 moles water at 20°C. Determine the lowering in the vapour pressure if the vapour pressure of pure water at 20°C is 17.5 torr. (Assume solution is an ideal)

Solution:

First we determine the mole fraction of glucose.

$$X_2 = \frac{n_2}{n_1 + n_2}$$

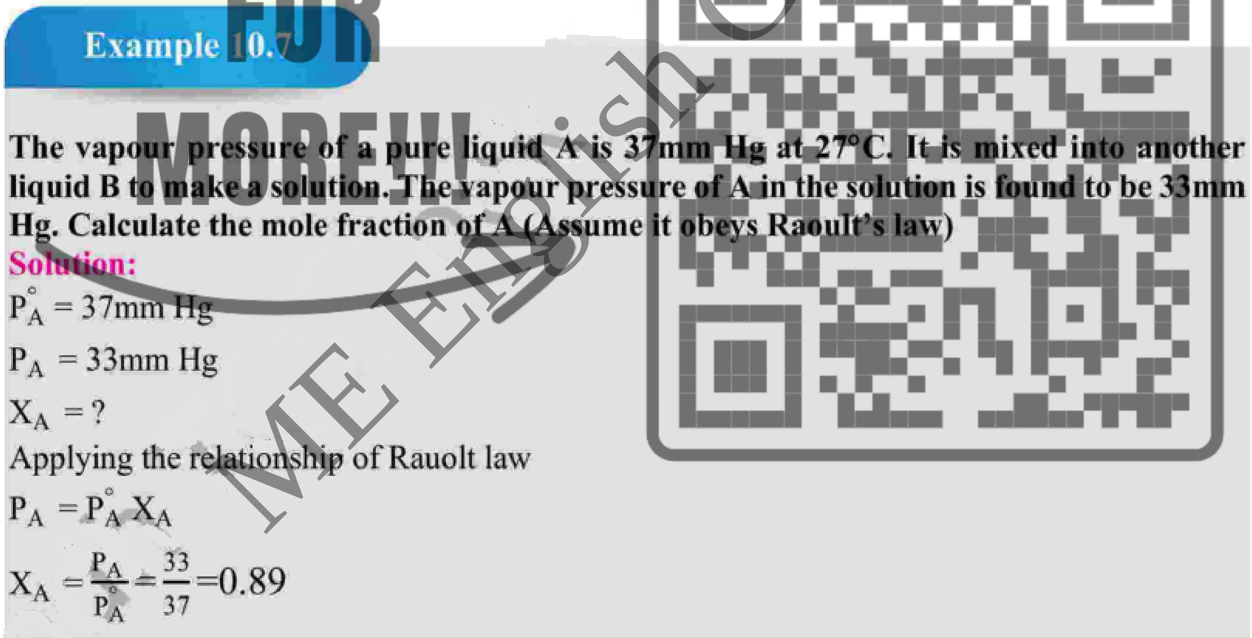
$$X_2 = \frac{0.15}{5.8 + 0.15} = 0.0252$$

Now applying second form of Raoult law

$\Delta P = P^\circ X_2$

$\Delta P = 17.5 \times 0.0252$

$\mathbf{\Delta P = 0.441\ torr}$



Example 10.7

The vapour pressure of a pure liquid A is 37mm Hg at 27°C. It is mixed into another liquid B to make a solution. The vapour pressure of A in the solution is found to be 33mm Hg. Calculate the mole fraction of A (Assume it obeys Raoult's law)

Solution:

$P_A^\circ = 37\text{mm Hg}$

$P_A = 33\text{mm Hg}$

$X_A = ?$

Applying the relationship of Rauolt law

$P_A = P_A^\circ X_A$

$X_A = \frac{P_A}{P_A^\circ} = \frac{33}{37} = 0.89$

Short Questions

1. Name various units of concentration and explain mole fraction.

Ans)

Various units of concentration:

1. Percentage Composition
2. Molarity (M)
3. Molality (m)
4. Mole Fraction (X)
5. Parts per million (ppm)
6. Parts per billion (ppb)
7. Parts per trillion (ppt)

Mole Fraction (X): This unit is used when two or more components are present in the solution. It is the ratio of number of moles of one component to that of all components of solution.

$X_A = \frac{\text{moles of substance A}}{\text{total moles of solution}}$ $X_B = \frac{\text{moles of substance B}}{\text{total moles of solution}}$

The sum of mole fractions of all the components of a solution is always a unity.

$$X_A + X_B = 1$$

For example if a solution is made up of 1 mole methanol in 4 moles water, the mole fraction of methanol will be 0.2 and water will be 0.8. Now if we add the mole fraction of both methanol and water we get unity.

$$X_{methanol} + X_{water} = 0.2 + 0.8 = 1$$

2. Define Molarity and molality. Which of these depends on temperature?

Ans)

Molarity (M): It is the number of moles of solute dissolved per dm³ of solution.

Molality (m): It is the number of moles of solute per kilogram of solvent.

- Molarity is temperature dependent while molality not.

3. Explain on particles bases how the vapours pressure of solution is lowered by adding non volatile solute.

Ans) Adding a non-volatile solute to a solvent reduces the vapor pressure of the solution. This happens because the solute particles disrupt the normal process of solvent molecules escaping into the gas phase. As a result, fewer solvent molecules vaporize, leading to a lower vapor pressure in the solution compared to the pure solvent. This phenomenon is described by Raoult's Law.

4. What are miscible and immiscible liquids? Why n-hexane (petrol) is immiscible in water?

Ans)

Miscible Liquids: Miscible liquids are those that can mix together in any proportion to form a homogeneous solution.

Example: An example of miscible liquids is ethanol and water. When you mix them, they form a single, uniform solution with no separate layers.

Immiscible Liquids: Immiscible liquids are the opposite of miscible liquids. These are liquids that cannot mix together to form a homogeneous solution, and they tend to separate into distinct layers when combined.

Example: Example of immiscible liquids is oil and water. When you mix them, they separate into two distinct layers, with the oil floating on top of the water.

The reason of n-hexane (petrol) is immiscible in water: n-Hexane (petrol) is immiscible in water because it is a nonpolar molecule, while water is highly polar. The difference in polarity and intermolecular forces prevents them from mixing, causing them to separate into distinct layers when combined. This immiscibility is due to the "like dissolves like" principle in chemistry.

5. Solubility of oxygen in water increases with pressure but solubility of glucose in water has negligible effect of pressure why?

Ans) The solubility of oxygen in water increases with pressure due to Henry's Law, which states that gas solubility is directly proportional to gas pressure. In contrast, the solubility of solids like glucose in water is minimally affected by pressure because pressure changes have little impact on the solubility of solids in liquids, which is mainly influenced by temperature and the nature of solute-solvent interactions.

Descriptive Questions

1. State Raoult's law and derive its mathematical expression

Ans)

Raoult's law:

Statement: For a nonvolatile solute system it states as "the vapours pressure of a solution which is a made up of nonvolatile solute with volatile solvent is directly proportion to the mole fraction of solvent".

Derivation:

$$P \propto X_1$$

$$P = P^o X_1 \text{ ……….. (i)}$$

Here **P** specifies the vapours pressure of solution, **P^o** represents vapours pressure of solvent and **X_1** is the mole fraction of solvent.

Since in a binary solution $X_1 + X_2 = 1$, hence $X_1 = 1 - X_2$

$$P = P^o (1 - X_2)$$

$$P = P^o - P^o X_2$$

$$P – P = P^o X_2$$

$$\Delta P = P^o X_2 \text{ ……. (ii)}$$

Equation (ii) represents the second form of Raoult's law which states as the lowering of vapour pressure is directly proportional to the mole fraction of solute.

$$\frac{\Delta P}{P^o} = X_2 \text{ ………(iii)}$$

Here $\frac{\Delta P}{P^o}$ is referred as relative lowering in vapours pressure.

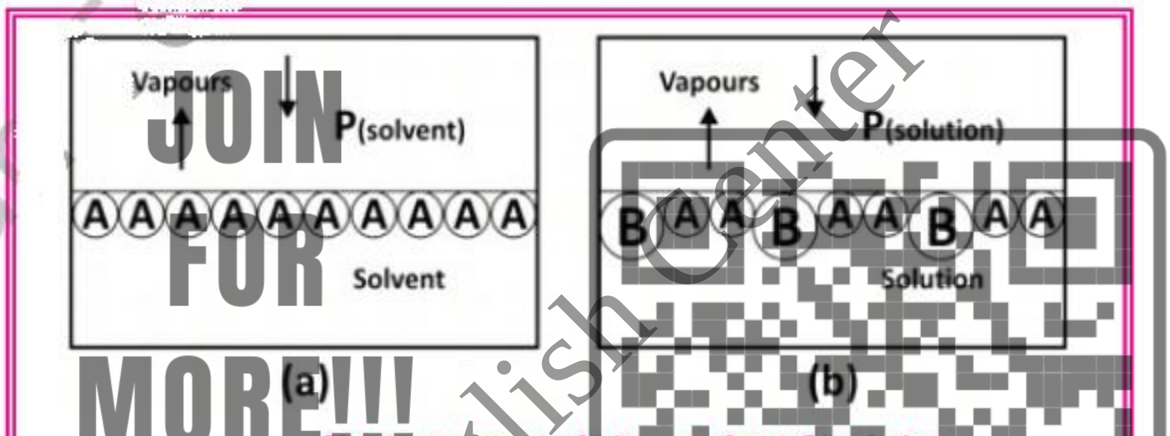
Eq. (iii) represents third form of Raoult's law which states as the relative lowering of vapours pressure is equal to the mole fraction of solute.

Raoult's law is also applicable on a binary solution made up of two miscible volalite liquids having similar order of polarity and molecular size. The partial pressure of each liquid in the mixture is equal to the vapours pressure of pure component multiplied by its mole fraction and may be written as

$$P_A = P^o_A X_A \text{ and } P_B = P^o_B X_B$$

Thus the total pressure of solution is equal to the sum of partial pressure of both liquid in the mixture.

$$P_t = P^o_A X_A + P^o_B X_B$$



Vapours pressure of (a) pure solvent (b) solution

2. What does an Ideal solution means? Give four characteristics to distinguish between ideal and non ideal solution.

Ans)

Ideal solution: An ideal solution, in the context of chemistry, refers to a homogeneous mixture of two or more substances (usually liquids or gases) in which the behavior of the mixture closely follows Raoult's Law.

Example: Example of liquid pair which form ideal solution on mixing are methanol ethanol, benzene-toluene etc.

Characteristics to distinguish between ideal and non ideal solution: To distinguish between ideal and non-ideal solutions, you can look for the following four characteristics:

1. **Raoult's Law Deviation:** In ideal solutions, the observed vapor pressure closely follows Raoult's Law. In non-ideal solutions, there may be deviations from

Raoult's Law, with vapor pressures either higher (positive deviation) or lower (negative deviation) than predicted by Raoult's Law.

2. **Interaction Forces:** In ideal solutions, the intermolecular forces between like molecules (e.g., solvent-solvent and solute-solute interactions) are similar in strength to the intermolecular forces between unlike molecules (e.g., solvent-solute interactions). In non-ideal solutions, there can be significant differences in intermolecular forces, leading to deviations from ideal behavior. For example, if solute-solute interactions are stronger than solvent-solute interactions (negative deviations), the solution may have lower vapor pressures than expected by Raoult's Law.
3. **Heat of Mixing:** Ideal solutions do not exhibit heat effects upon mixing; there is no heat absorbed or released. In contrast, non-ideal solutions can exhibit either endothermic (heat absorbed) or exothermic (heat released) behavior upon mixing, depending on the nature of intermolecular forces.
4. **Composition Range:** Ideal solutions are characterized by a wide range of solubilities where mixing occurs without significant changes in properties. Non-ideal solutions may have limited solubility ranges where mixing results in significant property deviations. In some cases, phase separation may occur if solubility limits are exceeded, indicating non-ideal behavior.

3. Define osmosis and osmotic pressure. Give four daily life examples of osmosis.

Ans) Osmosis: It is the movement of solvent molecules (usually water) through a semipermeable membrane from an area of lower solute concentration to an area of higher solute concentration.

Osmotic pressure: It is the pressure exerted by a solvent as it flows through a semipermeable membrane to equalize the solute concentration on both sides of the membrane.

Daily life examples of Osmosis:

1. Due to bacterial infection or certain other reasons, swelling and bursting of RBCs takes place in blood stream. This biochemical process is known as heamolysis. Literally, heamolysis is endo osmosis during which water pass through semi permeable membrane of RBCs and destroy them.
2. Fresh water fish absorb water through their semi permeable skin because their body fluid is much saltier than the water in which they swim.

3. Although plant absorbs water through their entire surface including root, leaves and stem, however it mainly occur by root hairs through the process of osmosis.
4. Food after digestion in various region of alimentary canal change into chyme which then absorb into body tissues through the semi permeable wall of small intestine.

4. What are colligative properties? Why does the boiling point of a liquid get raised when a non volatile salute is added?

Ans)

Colligative properties:

Definition: Certain physical properties of solutions depends upon the number of solute particles rather than its chemical nature, these are referred as colligative properties.

Examples: Examples are lowering of vapours pressure, elevation of boiling point, depression of freezing point and osmotic pressure.

Elevation of boiling point of a liquid by the addition of non volatile salute: Here's a simplified explanation of why the boiling point rises.

1. **Reduction of effective concentration of the solvent molecules at the surface:** When a non-volatile solute is added to a solvent, the solute molecules occupy some of the space at the surface of the solution. This means that the effective concentration of the solvent molecules at the surface is reduced compared to that in a pure solvent.
2. **Reduced Vapor Pressure:** According to Raoult's Law, the vapor pressure of a component is directly related to its concentration. In this case, the reduced effective concentration of the solvent at the surface results in a lower vapor pressure for the solvent in the solution compared to the vapor pressure of the pure solvent.
3. **Higher Boiling Point:** The boiling point of a liquid is the temperature at which its vapor pressure equals the atmospheric pressure. Since the vapor pressure of the solvent is reduced in the presence of a non-volatile solute, the solution will need to be heated to a higher temperature to reach the vapor pressure necessary for boiling to occur. Therefore, the boiling point of the solution is elevated.

5. Differentiate among true solution, colloidal solution and suspension on the bases of

(i) Particle size **(ii) Visibility**

Ans)

Characteristic	True Solution	Colloidal Solution	Suspension
Particle Size	< 1 nanometers (10^{-9} meters)	1 nanometer to 1 micrometer (10^{-9} to 10^{-6} meters)	> 1 micrometer (10^{-6} meters)
Visibility	Transparent and optically clear	Translucent or milky; exhibits the Tyndall effect	Cloudy or turbid; scatters light

Numerical Questions

1. Automotive antifreeze is a 60% (w/w) aqueous solution of ethylene glycol ($C_2H_6O_2$). Determine (a) molality of solution (b) mole fraction of ethylene glycol in the solution.

Data:

60% (w/w) aqueous solution of ethylene glycol ($C_2H_6O_2$)

(a) Molality of solution = ?

(b) Mole fraction of ethylene glycol = ?

Solution:

(a)

(i) 60% aqueous solution of ethylene glycol ($C_2H_6O_2$) represents 60g ethylene glycol in 100g solution thus the mass of water is calculated as

Mass of water in gram = 100 - 60 = 40g

Mass of water in kg = $\frac{40}{1000}$ = 0.04 kg

(ii) No. of moles of ethylene glycol = $\frac{\text{mass of ethylene glycol}}{\text{molar mass of ethylene glycol}}$

No. of moles of ethylene glycol = $\frac{60}{62}$ = 0.97 moles

(iii) Molality of solution = $\frac{\text{moles of ethylene glycol}}{\text{mass of water (kg)}}$

Molality of solution = $\frac{0.97}{0.04}$ = 24.25 mol/kg

(b)

First we determine the number of moles of ethylene glycol and water from their given masses

Moles of water = n_1 = $\frac{40}{18}$ = 2.222 moles

Moles of ethylene glycol = n_2 = $\frac{60}{62}$ = 0.97 moles

Mole fraction of ethylene glycol = $\frac{n_2}{n_1 + n_2}$ = $\frac{0.97}{2.222 + 0.97}$ = 0.3

2. A solution is prepared by mixing 46g ethanol (C_2H_5OH) and 180g water. Calculate the mole fraction of both components.

Data:

Mass of ethanol = 46 g

Mass of water = 180 g

Mole fraction of water = X_1 = ?

Mole fraction of ethanol = X_2 = ?

Solution:

First we determine the number of moles of ethanol and water from their given masses

Moles of water = n_1 = $\frac{180}{18}$ = 10 moles

Moles of ethanol = n_2 = $\frac{46}{46}$ = 1 moles

Mole fraction of water = X_1 = $\frac{n_1}{n_1 + n_2}$ = $\frac{10}{10 + 1}$ = 0.909

Mole fraction of ethanol = X_2 = $\frac{n_2}{n_1 + n_2}$ = $\frac{1}{10 + 1}$ = 0.090

Chapter 11: THERMOCHEMISTRY

Multiple Choice Questions

1. **Choose the correct answer:**

(i) Least entropy found in which of the following state of water:

(a) Liquid water at 4°C (b) Liquid water at 25°C

(c) Steam at 100°C (c) Steam at 100°C

(ii) The energy corresponds to the given thermochemical process is labeled as:

$$Li^{+}_{(g)} + \bar{C}l_{(g)} \longrightarrow LiCl_{(s)}$$

(a) Ionization energy (b) Lattice energy

(b) Lattice energy (b) Lattice energy

(iii) Which of the following change is not an endothermic reaction:

(a) Decomposition of lime (b) Cracking of alkanes

(c) Combustion of butane (d) Photosynthesis

(iv) Heat transfer cannot be feasible across the boundary of a:

(a) Open system (b) Close system

(c)Isolated system (d) Thermo permeable system

(v) Which of the following enthalpy change is always negative:

(a) Enthalpy of formation (b) Enthalpy of decomposition

(c) Enthalpy of combustion (d) Enthalpy of reaction

(vi) Standard enthalpy of formation of all of the following elements at 25°C and 1 atm pressure are zero except:

(a) $C_{(diamond)}$ (b) $C_{(graphite)}$

(c) O_2 (d) N_2

(vii) In the equation of First law of thermodynamics (AE = q + w), the property(s) which depends upon initial and final state is (are):

(a) ΔE (b) q

(c) W (d) Both q and W

(viii) Which statement is incorrect:

(a) For constant pressure process, $\Delta H = \Delta E + P\Delta V$

(b) For constant volume process, $\Delta E = q$

(c) For exothermic reactions, $\Delta H > 0$

(d) For Hess law $\Sigma\Delta H^o_{(cycle)} = 0$

(ix) In a thermochemical process, no work is done if the system is kept at:

(a) Constant temperature (b) Constant pressure

(c) Constant volume (d) Constant mass

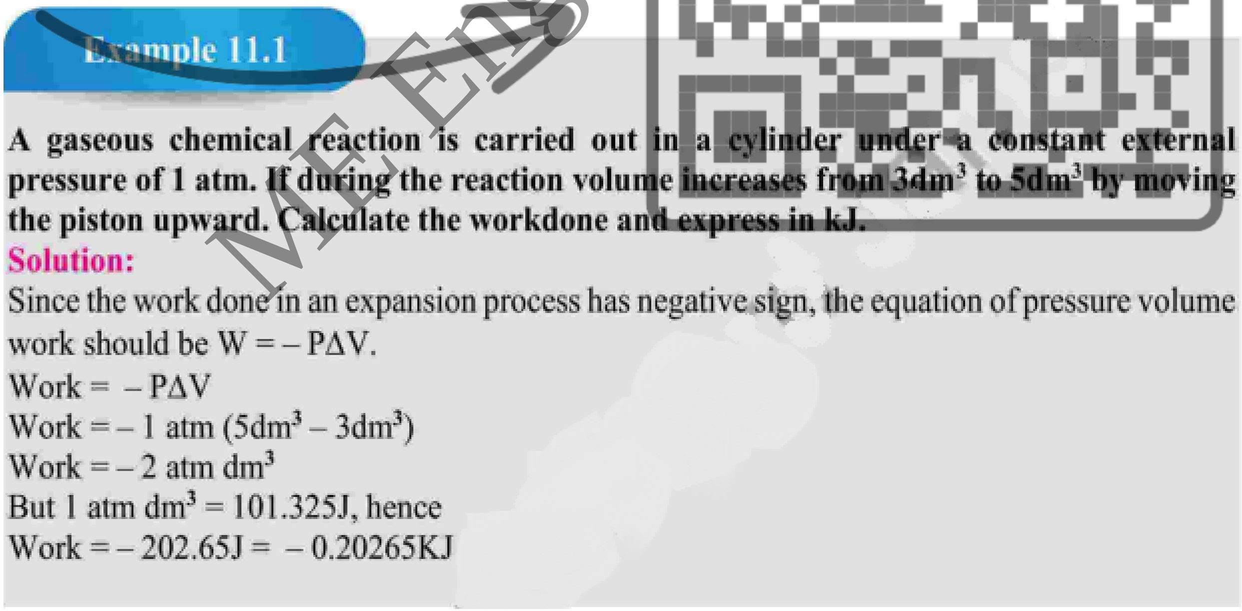
(x) Volume is a:

(a) State function (b) Path function

(c) Intensive properties (d) Colligative property

Key:

(i) d	(ii) b	(iii) c	(iv) c	(v) c
(vi) a	(vii) a	(viii) c	(ix) c	(x) a



Example 11.1

A gaseous chemical reaction is carried out in a cylinder under a constant external pressure of 1 atm. If during the reaction volume increases from 3dm^3 to 5dm^3 by moving the piston upward. Calculate the workdone and express in kJ.

Solution:

Since the work done in an expansion process has negative sign, the equation of pressure volume work should be $W = -P\Delta V$.

Work = $-P\Delta V$

Work = -1 atm (5dm^3 – 3dm^3)

Work = -2 atm dm^3

But 1 atm dm^3 = 101.325J, hence

Work = -202.65J = -0.20265KJ

Example 11.2

Burning of petrol in an automobile engine gives carbondioxide and water vapours. If the gases do 675J work in pushing the piston outward and the system lose 435J heat to the surrounding, calculate the internal energy change in kJ.

Solution:

Since heat is given out, the value of **q** is taken with negative sign. Likewise sign of **W** is also taken negative because work is done by the system.

$q = -435J$

$W = -675J$

$\Delta E = ?$

$\Delta E = q + w$

$\Delta E = (-435) + (-675)$

$\Delta E = -1110J$

$\Delta E = -1.11KJ$

Example 11.3

Calculate the enthalpy of combustion of propane at 25°C by the given informations.

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)} \qquad (\Delta H^\circ = ?)$$

ΔH_f° of $C_3H_{8(g)} = -103.9KJ/mol$

ΔH_f° of $CO_{2(g)} = -393.5KJ/mol$

ΔH_f° of $H_2O_{(\ell)} = -285.8KJ/mol$

Solution:

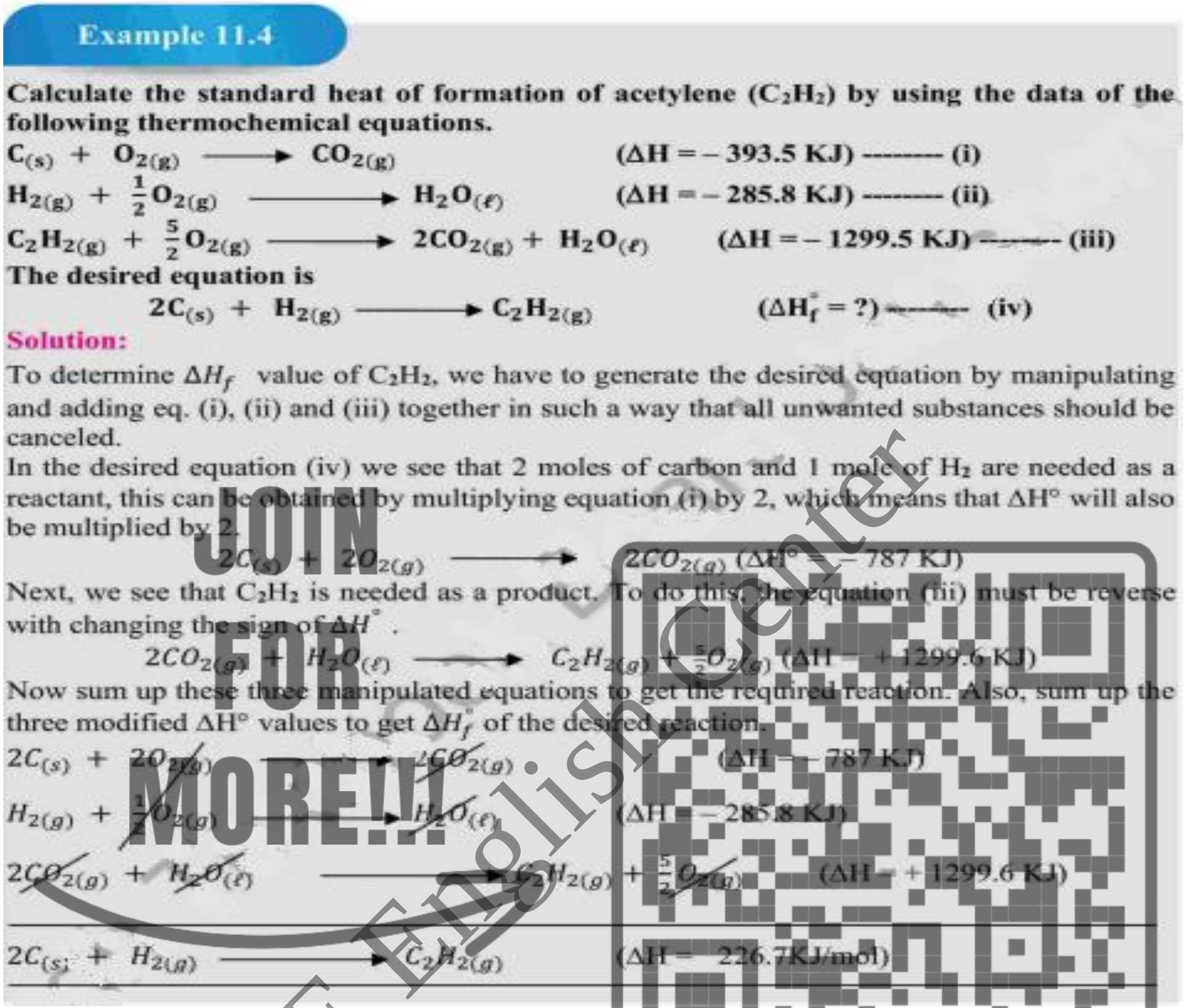
The mathematical form of heat of reaction ΔH° is given as.

$$\Delta H^\circ_{reaction} = \left[\left(\Sigma\, np\, \Delta H^\circ_{f\,(products)}\right) - \left(\Sigma\, nr\, \Delta H^\circ_{f\,(reactants)}\right) \right]$$

Substituting the values.

$$\Delta H^\circ_{reaction} = \left[(-393.5 \times 3) + (-285.8 \times 4)\right] - \left[(-103.9 \times 1)\right]$$

$$\Delta H^\circ_{reaction} = -2219.8\ KJ/mol$$



Example 11.4

Calculate the standard heat of formation of acetylene (C_2H_2) by using the data of the following thermochemical equations.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad (\Delta H = -393.5\ KJ) \text{ -------- (i)}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \qquad (\Delta H = -285.8\ KJ) \text{ -------- (ii)}$$

$$C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(\ell)} \qquad (\Delta H = -1299.5\ KJ) \text{ -------- (iii)}$$

The desired equation is

$$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)} \qquad (\Delta H_f^\circ = ?) \text{ -------- (iv)}$$

Solution:

To determine ΔH_f value of C_2H_2, we have to generate the desired equation by manipulating and adding eq. (i), (ii) and (iii) together in such a way that all unwanted substances should be canceled.

In the desired equation (iv) we see that 2 moles of carbon and 1 mole of H_2 are needed as a reactant, this can be obtained by multiplying equation (i) by 2, which means that ΔH° will also be multiplied by 2.

$$2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} \quad (\Delta H^\circ = -787\ KJ)$$

Next, we see that C_2H_2 is needed as a product. To do this, the equation (iii) must be reverse with changing the sign of ΔH° .

$$2CO_{2(g)} + H_2O_{(\ell)} \longrightarrow C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \quad (\Delta H = +1299.6\ KJ)$$

Now sum up these three manipulated equations to get the required reaction. Also, sum up the three modified ΔH° values to get ΔH_f° of the desired reaction.

$$2C_{(s)} + \cancel{2O_{2(g)}} \longrightarrow \cancel{2CO_{2(g)}} \qquad (\Delta H = -787\ KJ)$$

$$H_{2(g)} + \cancel{\frac{1}{2}O_{2(g)}} \longrightarrow \cancel{H_2O_{(\ell)}} \qquad (\Delta H = -285.8\ KJ)$$

$$\cancel{2CO_{2(g)}} + \cancel{H_2O_{(\ell)}} \longrightarrow C_2H_{2(g)} + \cancel{\frac{5}{2}O_{2(g)}} \qquad (\Delta H = +1299.6\ KJ)$$

$$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)} \qquad (\Delta H = 226.7 KJ/mol)$$

Example 11.5

Use the data provided below for the formation of $RbCl_{(s)}$, write thermochemical equations for all the steps involved in the Born Haber cycle and determine the enthalpy of formation of $RbCl_{(s)}$.

Sublimation energy of $Rb_{(s)}$ = 82 KJ/mol

Ionization energy of $Rb_{(g)}$ = 403 KJ/mol

Dissociation energy of $Cl_{2(g)}$ = 242 KJ/mol

Electron affinity of $Cl_{(g)}$ = -348.5 KJ/mol
Lattice energy of RbCl = -689 KJ/mol

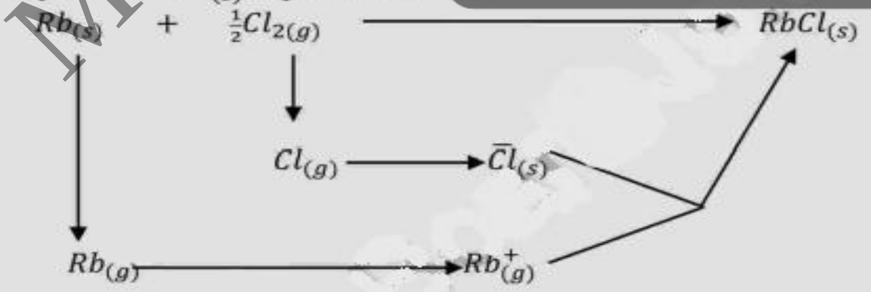
Solution:

Since, according to Hess's law overall enthalpy change of a cyclic thermochemical process is zero, the sum up of all five steps involved in the process will get heat of formation of RbCl. Thermochemical equations associated with Born Haber cycle in the formation of $RbCl_{(s)}$ maybe written as

$$Rb_{(s)} \longrightarrow Rb_{(g)} \qquad (\Delta H^\circ_{(sub)} = 82KJ/mol)$$
$$Rb_{(g)} \longrightarrow Rb^+_{(g)} \qquad (\Delta H^\circ_{(IE)} = 403KJ/mol)$$
$$\tfrac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad (\Delta H^\circ_D = \tfrac{1}{2} \times 242KJ/mol)$$
$$Cl_{(g)} \longrightarrow \bar{C}l_{(g)} \qquad (\Delta H^\circ_{EA} = -348.5KJ/mol)$$
$$Rb^+_{(g)} + \bar{C}l_{(g)} \longrightarrow RbCl_{(s)} \qquad (\Delta H^\circ_{LE} = -689KJ/mol)$$

$$Rb_{(s)} + \tfrac{1}{2}Cl_{2(g)} \longrightarrow RbCl_{(s)} \qquad (\Delta H^\circ_f = -431.5KJ/mol)$$

The Born Haber cycle on $RbCl_{(s)}$ is presented below



Heat of formation of RbCl(s) may also be calculated by summing up the individual steps involved in the following simple way.

$$\Delta H^\circ_f = \Delta H_{sub} + \Delta H_{IE} + \tfrac{1}{2}\Delta H_D + \Delta H_{EA} + \Delta H_{LE}$$
$$\Delta H^\circ_{f(RbCl)} = (82) + (403) + (\tfrac{1}{2} \times 242) + (-348.5) + (-689)$$
$$\Delta H^\circ_{f(RbCl)} = -431.5\ Kj/mol$$

Short Questions

1. State precisely the meaning of each of the following terms.

(i) System and surrounding **(ii) State and state function**

(iii) Internal energy and Enthalpy

Ans)

(i)

System: It is a distinct part of our universe which is under particular experimental debate and separated from surrounding by an imaginary or real surface and can change its shape or size is called a system.

Surroundings: Everything outside the arbitrarily selected boundaries of the system that affects the system or is affected by it is called surrounding.

(ii)

State of System: A thermodynamic system is said to be in a certain state if some macroscopic properties such as temperature pressure, volume, and moles are known. With the change of one or more of these macroscopic properties, the system changes its state.

State Function: A state function is thermodynamic parameter which is dependent on initial and final state of the system and is independent of how the change is occurred.

(iii)

Enthalpy of a System: It defines as "the sum of internal energy and algebraic product of its pressure and volume".

Internal Energy: The total energy content of a thermodynamic system under a given set of conditions is known as internal energy.

2. What is meant by Internal energy change (ΔE) and Enthalpy change (ΔH)? Under what conditions are ΔE and ΔH equal?

Ans) Internal energy change (ΔE): The internal energy change, denoted as ΔE (pronounced "delta E"), represents the change in the total internal energy of a system as it undergoes a physical or chemical process.

Enthalpy change (ΔH): Enthalpy change (ΔH), often referred to as the heat of reaction or heat of reaction change, is a thermodynamic concept that represents the change in enthalpy of a system as it undergoes a chemical reaction at constant pressure.

- For the reaction in which one or more solids or liquids are involved, the value of PΔV becomes almost zero because solids and liquids undergo very small volume change. Thus in this case enthalpy change (ΔH) will be equal to internal energy change (ΔE).

3. How can you define standard enthalpy of formation and standard enthalpy of reaction.

Ans)

Standard enthalpy of formation: It defines as "the enthalpy change of a chemical reaction in which one mole of a pure substance is formed from its elements with all substance in their standard state".

Standard enthalpy of reaction: It is the enthalpy absorbed or evolved when fixed number of moles of reactants as represented in a balance chemical equation are completely reacted to form product with the condition that all reactants and products are in their standard states.

Descriptive Questions

1. State and explain First law of Thermodynamics. Derive pressure-volume work of a system.

Ans)

First law of thermodynamics:

Statement: "In any physical or chemical process, the net energy of a system and its surroundings must remain constant".

Explaination: To develop the mathematical approach of the law let us consider a system in its initial state having internal energy $\mathbf{E_1}$. If "**q**" be the heat supplied to the system while **W** be the work done on the system, the internal energy increases to $\mathbf{E_2}$. Then according to the law, the internal energy change (E_2-E_1) may be formulated as

$$\Delta E = q + w$$

The sign of '**q**' is taken positive if thermochemical process is concerned with heat absorption but in case of heat release it is taken as negative sign. The sign of **W** should be taken negative for thermochemical expansion and positive if it undergoes compression.

Derivation of Pressure-Volume Work Equation: Mechanical work due to expanding or squeezing of a system at constant external pressure is known as pressure-volume work.

Consider a gas confined in a cylinder fitted by a negligible weight, friction less and movable piston of cross-section area **A** at a constant external pressure. If the force exerted by the gas on the inner wall of the piston is greater than external pressure, the piston moves upward from a height h_1 to h_2 and hence does some work which may be formulated as

$$W = -F(h_2 - h_1) \text{ ………(1)}$$

Insertion of a negative sign indicates that external pressure opposes the expansion of gas.

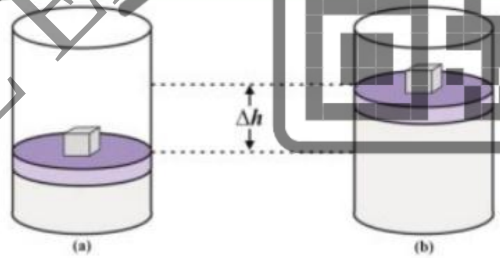
Since $P = F/A \quad \Rightarrow \quad F = P.A$

Put $F = P.A$ in equation (1)

$$W = -PA(\Delta h)$$

But $A.\Delta h$ represents volume change (ΔV) of the system so work done on thermodynamics system is deduced as

$$W = -P\Delta V$$



pressure-volume work in thermodynamic expansion process (a) volume at initial state (b) volume at the final state

3. State and explain Hess's Law of enthalpy summation. Discuss its applications.

Ans)

Statement: This law states as “if a chemical reaction can be brought about in more than one path way, the net enthalpy change is the same provided that the initial and final states are the same".

Explanation: Let us suppose a substance A is converted to Z by two different paths as illustrated in following figure. It may either change directly to Z in one step or by involving some intermediate steps in which X and Y are formed. In both cases the total enthalpy change remains the same.

$$\text{Path-1} = A \xrightarrow{\Delta H} Z$$

$$\text{Path-2} = A \xrightarrow{\Delta H_1} X \xrightarrow{\Delta H_2} Y \xrightarrow{\Delta H_3} Z$$

$$\text{Thus } \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

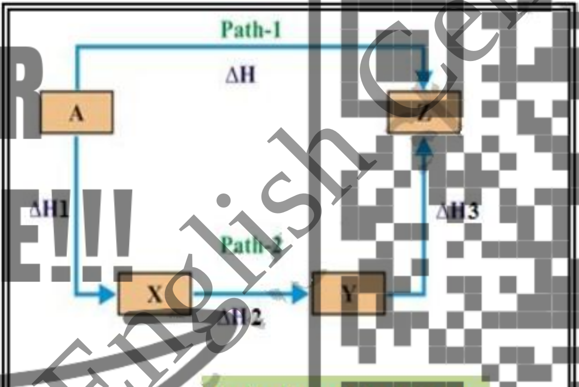


Illustration of Hess's Law

Uses/applications of Hess’s law:

(1) The determination of heat of reaction: There are two ways to calculate ΔH° of a reaction. It either determined calorimetrically or calculate from known values of ΔH^o_f of all the susbstances involve in the reaction. Hess's law provides us a convenient way to find out the heat change involves in a chemical reaction by subtracting the sum of heat of formation of all reactants from the sum of heat of formation of all products.

(2) The determination of heat of formation: Realizing the fact that thermochemical equations can be added subtracted or multiplied like ordinary algebraic equations, Hess's law is useful to calculate the heat of formation of many compounds where an experimental determination is not possible.

To understand how is Hess's Law useful in thermochemistry, look at the oxidation of sulphur to sulphur trioxide.

$$S_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

Analyzing the reaction, we find that sulphur can not be directly oxidized into SO_3, therefore ΔH^o_f of SO_3 can not be determined if we put sulphur and oxygen in a calorimeter. The only option is to go for an alternative route which consists of following two steps.

$$\text{Step-1: } S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \ (\Delta H_1 = -296.8KJ/mol)$$
$$\text{Step-2: } SO_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)} \ (\Delta H_2 = -99.2KJ/mol)$$

Thus the ΔH^o_f of $SO_{3(g)}$ is indirectly determined by adding enthalpy change of step 1 and step 2.

$$\begin{array}{lll} S_{(s)} + O_{2(g)} \longrightarrow & SO_{2(g)} & (\Delta H_1 = -296.8KJ/mol) \\ SO_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow & SO_{3(g)} & (\Delta H_2 = -99.2KJ/mol) \\ \hline S_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow & SO_{3(g)} & (\Delta H^\circ_f = -396KJ/mol) \end{array}$$

4. Explain Exothermic and Endothermic reactions with the help of the energy diagram.

Exothermic Reactions: Exothermic reactions (Exo; out) are those in which heat is given out making the surrounding warmer. In the course of exothermic reactions, energy stored in the chemical bond of products is less than reactant hence these reactions are energetically favorable and often occur spontaneously but sometimes we need extra energy to get them started. The overall energy released in these reactions is represented by AH with a negative sign.

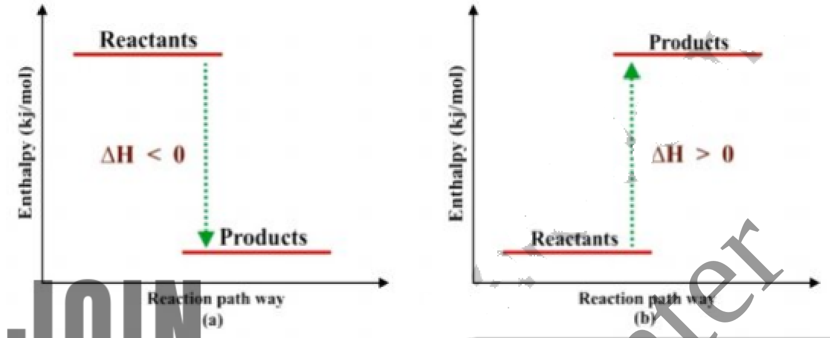
Example: All combustion reactions including the burning of fuel and coal, oxidation of Sui gas, etc are exothermic reactions and can easily be noted by a rise of the surrounding temperature.

$$C + O_2 \longrightarrow CO_2 \ (\Delta H = -ve)$$
$$CH_4 + 2O_2 \longrightarrow 2CO_2 + 2H_2O \ (\Delta H = -ve)$$

Endothermic Reactions: Endothermic reactions (endo, taking in) are those in which heat is put into the system making the surrounding colder. In these reactions more energy is needed to break the bonds in the reactants than is released when new bonds are formed in the products. Since heat is used for the reaction to occur, these are referred to as non-spontaneous reactions. The net energy absorbed in these reactions is represented by AH with a positive sign.

Example: An appropriate endothermic reaction is photosynthesis during which plants absorb solar heat through their chlorophyll parts and this heat is utilized for the conversion of CO_2 and H_2O into glucose.

$$2CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \ (\Delta H = +ve)$$



Energy diagram of thermochemical reaction
(a) exothermic reaction (b) endothermic reaction

Numerical Questions

1. A thermochemical process is carried out at constant pressure of 8.52atm. If it absorbs of 15.4kJ energy from the surrounding due to which an expansion in the volume 4.7dm^3 is occurred. Calculate its change in internal energy.

Data:

q = + 15.4 kJ (Since heat is given in)

P = 8.52atm

$\Delta V = 4.7dm^3$

$\Delta E = ?$

Solution:

$W = -P\Delta V = (8.52)(4.7) = -40.044$ atm.dm^3 (Since work is done by the system)

But 1atm. dm^3 = 101.325 J

W = -40.044 x 101.325 = -4057.458 J = -4057.458/1000 = -4.057 kJ

$\Delta E = q + W$

$\Delta E = 15.4 + (-4.057 \text{ kJ}) = 11.34 \text{ kJ}$

2. Using the data in table 11.2, calculate the standard enthalpy change for each of the following reactions.

$$2H_2S_{(g)} + 3O_{2(g)} \longrightarrow 2H_2O_{(\ell)} + 2SO_{2(g)}$$
$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

Solution:

(a)

The mathematical form of heat of reaction ΔH^o(is given as

$\Delta H^o_{reaction}$ = (Σnp $\Delta H^o_{f(product)}$)-(Σnr $\Delta H^o_{f(reactants)}$)

$\Delta H^o_{reaction}$ = ((-285.8 x 2) + (-296.8 x 2))-(-20.17 x 2)

$\Delta H^o_{reaction}$ = -1124.86 kJ/mol

(b)

The mathematical form of heat of reaction ΔH^o(is given as

$\Delta H^o_{reaction}$ = (Σnp $\Delta H^o_{f(product)}$)-(Σnr $\Delta H^o_{f(reactants)}$)

$\Delta H^o_{reaction}$ = (-393.5 x 3) – ((-110.5 x 3) + (-824.2x 1))

$\Delta H^o_{reaction}$ = -24.8 kJ/mol

3. In the manufacturing of HNO_3 by the Ostwald process, one of the most important exothermic reactions is the oxidation of ammonia.

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(\ell)}$$

Determine standard heat of reaction (ΔH^o) from the following given data.

ΔH^o_f of $NH_{3(g)}$ = -46.19 kJ/mol

ΔH^o_f of $NO_{(g)}$ = 90.25 kJ/mol

ΔH^o_f of $H_2O_{(l)}$ = 285.8 kJ/mol

Solution:

The mathematical form of heat of reaction ΔH^o is given as

ΔH^o = (Σnp $\Delta H^o_{f(product)}$)-(Σnr $\Delta H^o_{f(reactants)}$)

ΔH^o = ((90.25 x 4) + (-285.8 x 6))-(-46.19 x 4)

ΔH^o = -1169.04 kJ/mol

4. Iso octane (C_8H_{18}) is an efficient fuel with a high octane rating. The combustion of C_8H_{18} in an internal combustion engine is represented in the following thermochemical equation. Find its standard heat of combustion.

$$C_8H_{18(\ell)} + 12\tfrac{1}{2}O_{2(g)} \longrightarrow 8CO_{2(g)} + 9H_2O_{(\ell)} \quad (\Delta H_f^{\circ} = ?)$$

Given that **$\Delta H^o{}_f$ of CO_2 = -393.5 KJ/mol**

$\Delta H^o{}_f$ of H_2O = -285.8 KJ/mol

$\Delta H^o{}_f$ of C_8H_{18} = -223.8 KJ/mol

Solution:

The mathematical form of heat of reaction ΔH^o(is given as

$\Delta H^o{}_{reaction}$ = (Σnp $\Delta H^o{}_{f(product)}$)-(Σnr $\Delta H^o{}_{f(reactants)}$)

$\Delta H^o{}_{reaction}$ = ((-393.5 x 8) + (-285.8 x 9))-(-223.8 x 1)

$\Delta H^o{}_{reaction}$ = -5496.4 kJ/mol

5. Glycerol ($C_3H_8O_3$) is a well known organic compound due to its versatile uses. Calculate the standard enthalpy of formation of Glycerol from the data given below.

$$3C_{(s)} + 4H_{2(g)} + \tfrac{3}{2}O_{2(g)} \longrightarrow C_3H_8O_{3(\ell)} \quad (\Delta H_f^{\circ} = ?)$$
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad (\Delta H^{\circ} = -393.5 \text{ KJ/mol})$$
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \quad (\Delta H^{\circ} = -285.8 \text{ KJ/mol})$$
$$C_3H_8O_{3(\ell)} + 3\tfrac{1}{2}O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(\ell)} \quad (\Delta H^{\circ} = -1654.1 \text{ KJ/mol})$$

Solution:

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2\,(g)}$ (ΔH^o = -393.5 kJ/mol) …….(1)

$H_{2(g)} + ½\, O_{2\,(g)} \longrightarrow H_2O_{\,(l)}$ (ΔH^o = -285.8 kJ/mol)………(2)

$C_3H_8O_{3(l)} + 7/2\ O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(l)}$ (ΔH^o = -1654.1 kJ/mol)………(3)

Multiply equation (1) by 3

$3C_{(s)} + 3O_{2(g)} \longrightarrow 3CO_{2\,(g)}$ (ΔH^o = -1180.5 kJ/mol) …….(4)

Multiply equation (2) by 4

$4H_{2(g)} + 2O_{2\,(g)} \longrightarrow 4H_2O_{\,(l)}$ (ΔH^o = -1143.2 kJ/mol)………(5)

Adding equation (4) and equation (5)

$3C_{(s)} + 4H_{2(g)} + 5O_{2(g)} \longrightarrow 3CO_{2\,(g)} + 4H_2O_{\,(l)}$ $(\Delta H^o = -2323.7$ kJ/mol)………(6)

Subtracting equation (3) from equation (6)

$3C_{(s)} + 4H_{2(g)} + 5O_{2(g)} \longrightarrow \cancel{3CO_2}_{\,(g)} + \cancel{4H_2O}_{(l)}$ $(\Delta H^o = -2323.7$ kJ/mol)

$- C_3H_8O_{3(l)} - 7/2\ O_{2(g)} \longrightarrow - \cancel{3CO_2}_{(g)} - \cancel{4H_2O}_{(l)}$ $(\Delta H^o = +1654.1$ kJ/mol)

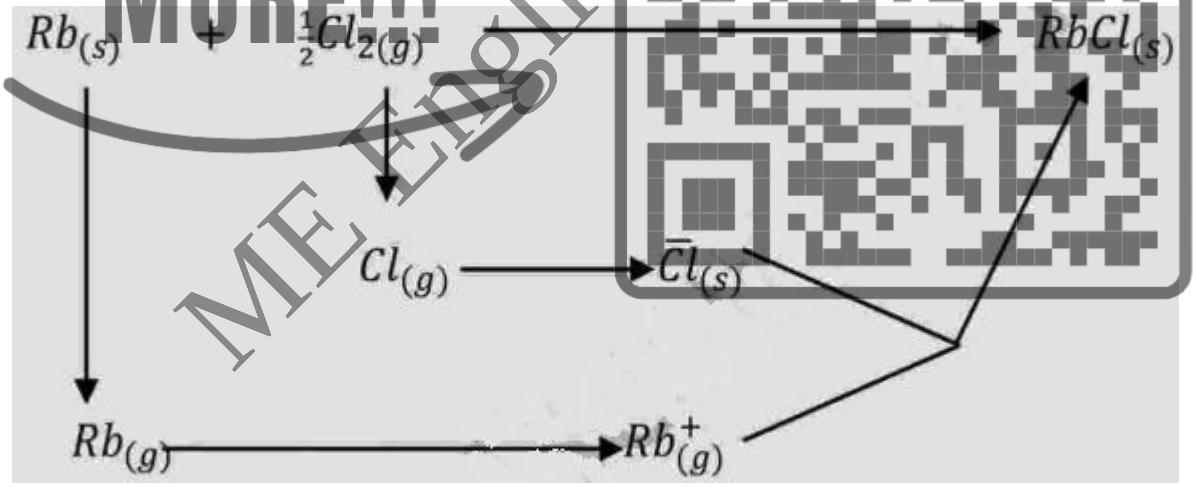
$3C_{(s)} + 4H_{2(g)} + 3/2\ O2_{(g)} \longrightarrow C_3H_8O_{3(l)}$ **$(\Delta H^o_f = -669.6$ kJ/mol)**

6. Draw a fully labeled Born Haber cycle for Rubidium chloride (RbCl) and determine the lattice energy by using the following values. (all in kJ/mol).

- **I.P$_{1st}$ of Rb = 403 kJ/mol**
- **Electron affinity of Cl = -349 kJ/mol**
- **Bond energy of Cl_2 = 242 KJ/mol**
- **Sublimation energy of Rb = 86.5 KJ/mol**
- **Heat of formation of $RbCl_{(s)}$ = -430.5 KJ/mol**

Solution:

The Born Haber cycle on RbCl(s) is represented below



Thermochemical equations associated with Born Haber cycle in the formation of RbCl may be written as

$Rb_{(s)} \longrightarrow Rb_{(g)}$ $(\Delta H^o_{(sub)} = 86.5$ KJ/mol)

$Rb(s) \longrightarrow Rb^+_{(g)}$ $(\Delta H^o_{(IE)} = 403$KJ/mol)

$\frac{1}{2}\ Cl_{2(g)} \longrightarrow Cl_{(g)}$ $(\Delta H^o_D = \frac{1}{2} \times 242 = 141$ KJ/mol)

$Cl_{(g)} \longrightarrow Cl^{-}_{(g)}$ $(\Delta H^{o}_{EA} = -349 KJ/mol)$

$Rb^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow RbCl_{(s)}$ $(\Delta H^{o}_{LE} = ?)$

$Rb + \frac{1}{2} Cl_2 \longrightarrow RbCl$ $(\Delta H^{o}_{f} = -430.5 \text{ KJ/mol})$

$\Delta H^{o}_{f} = \Delta H^{o}_{(sub)} + \Delta H^{o}_{(IE)} + \Delta H^{o}_{D} + \Delta H^{o}_{EA} + \Delta H^{o}_{LE}$

$-430.5 = 86.5 + 403 + 141 - 349 + \Delta H^{o}_{LE}$

$\boldsymbol{\Delta H^{o}_{LE} = -712 \text{ KJ/mol}}$

Chapter 12: ELECTROCHEMISTRY

Multiple Choice Questions

1. **Choose the correct answer**

(i) The outer body of dry cell serves as anode, it is made up of

(a) Copper (b) Zinc

(c) Lead (d) Iron

(ii) The conduction of electricity through an electrolytic solution is due to the flow of:

(a) Electrons (b) Ions

(c) Atoms (d) Molecules

(iii) During electrolysis, the reaction that takes place at anode is:

(a) Oxidation (b) Reduction

(c) Hydrolysis (d) Simultaneous oxidation and reduction

(iv) This statement is not correct for lead storage battery:

(a) It can be recharged (b) It is a primary battery

(c) Anode is made up of lead (d) Cathode is made up of lead oxide

(v) In Zn-SHE voltaic cell, the half reaction occurs at anode is:

(a) $Zn^{+2} + 2\bar{e} \longrightarrow Zn$ (b) $Zn \longrightarrow Zn^{+2} + 2\bar{e}$

(c) $2H^{+} + 2\bar{e} \longrightarrow H_2$ (d) $H_2 \longrightarrow 2H^{+} + 2\bar{e}$

(vi) The strongest oxidizing agent in the electro chemical series is:

(a) Li (b) H_2

(c) Cu (d) F_2

(vii) Galvanized rode of iron is coated with:

(a) Nickel (b) Zinc

(c) Chromium (d) Carbon

(viii) Fuel cell is a typical Galvanic cell which is based on the reaction between:

(a) Nitrogen and oxygen (b) Hydrogen and oxygen

(c) Methane and oxygen (d) Hydrogen and zinc

(ix) Oxidation number of Cr in $Na_2Cr_2O_7$ is:

(a)+3 (b)+6

(c) +8 (d) +12

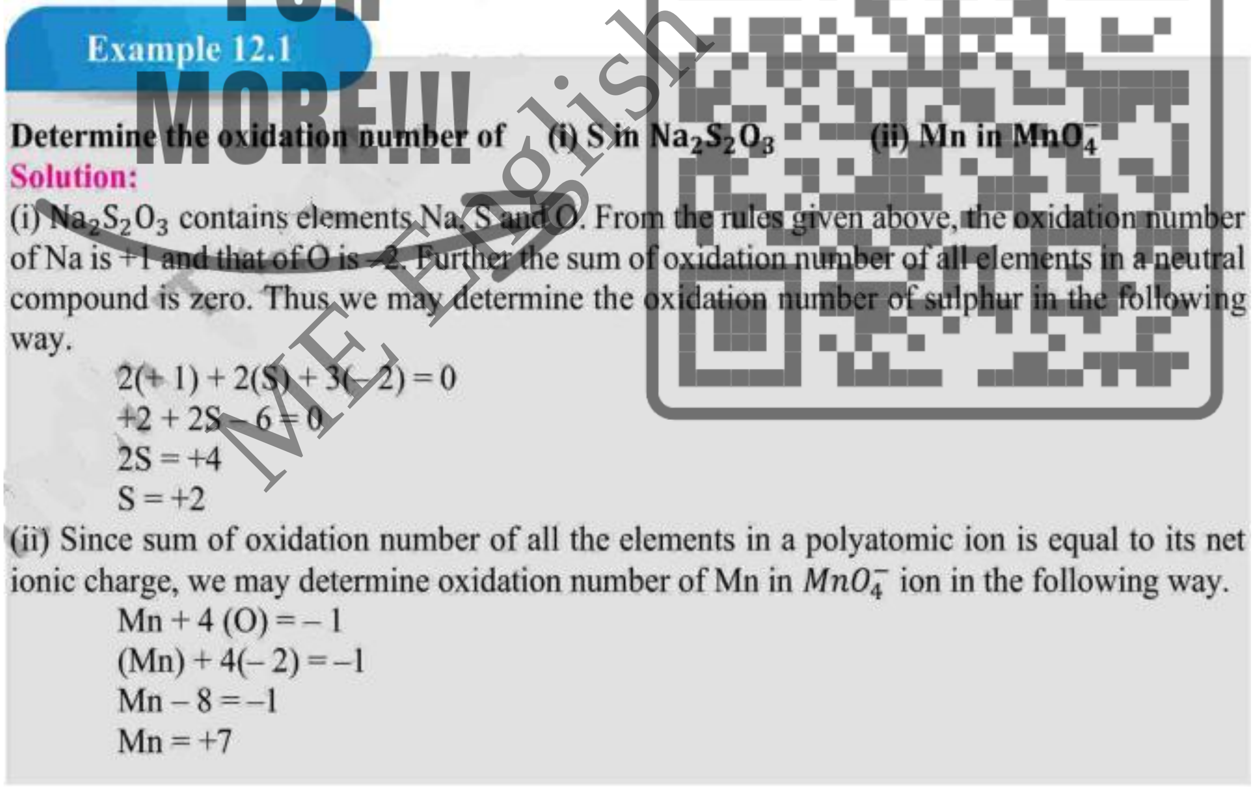
(x) Which of the following half cell reaction show oxidation:

(a) $Fe^{+3} \rightarrow Fe^{+2}$ (b) $Cl_2 \rightarrow 2Cl^-$

(c) $SO_4^{-2} \rightarrow SO_4^{-3}$ (d) $Zn \rightarrow Zn^{+2}$

Key:

(i) b	(ii) b	(iii) a	(iv) b	(v) b
(vi) d	(vii) b	(viii) b	(ix) b	(x)d



Example 12.1

Determine the oxidation number of (i) S in $Na_2S_2O_3$ (ii) Mn in MnO_4^-

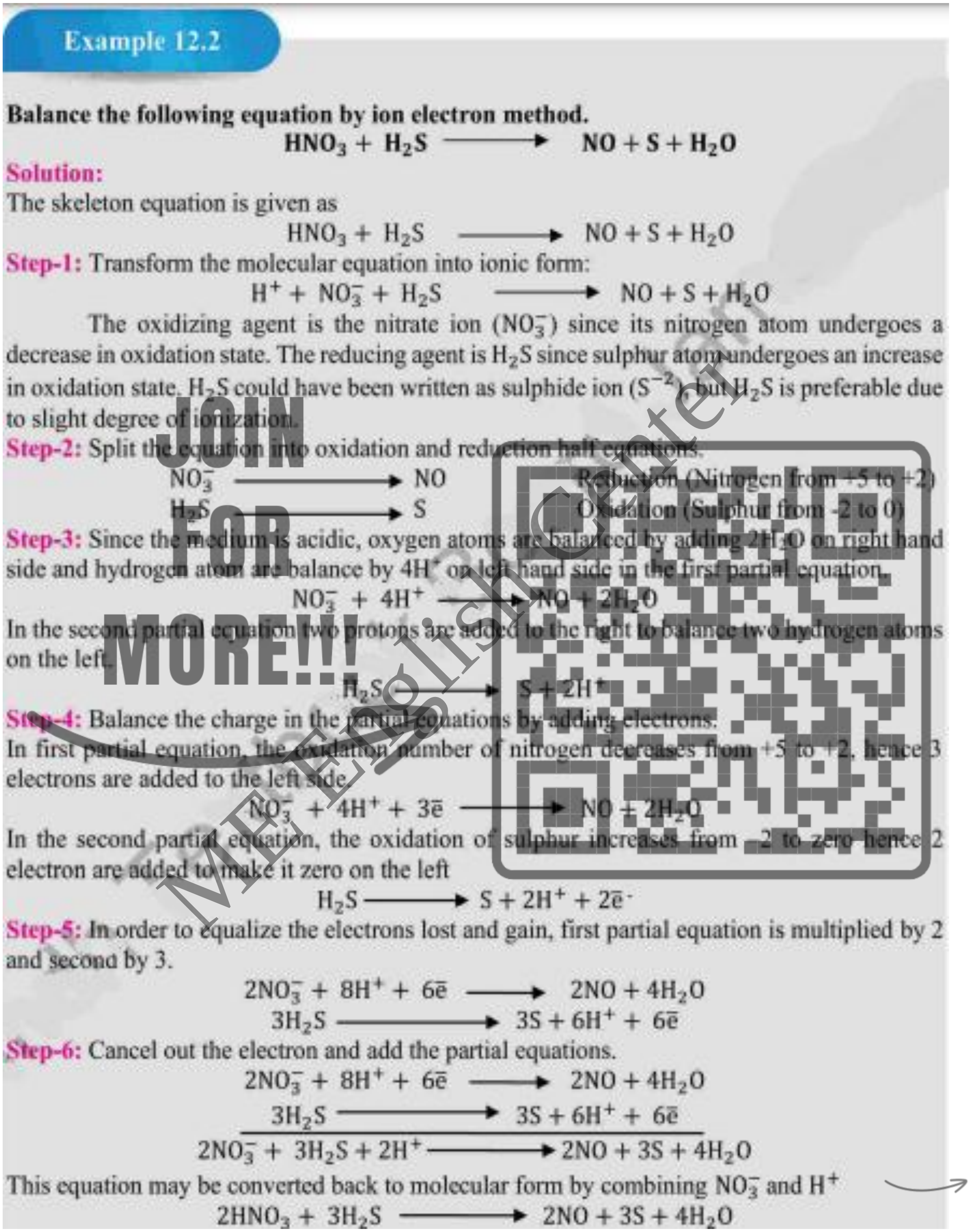
Solution:

(i) $Na_2S_2O_3$ contains elements Na, S and O. From the rules given above, the oxidation number of Na is +1 and that of O is −2. Further the sum of oxidation number of all elements in a neutral compound is zero. Thus we may determine the oxidation number of sulphur in the following way.

$$2(+1) + 2(S) + 3(-2) = 0$$
$$+2 + 2S - 6 = 0$$
$$2S = +4$$
$$S = +2$$

(ii) Since sum of oxidation number of all the elements in a polyatomic ion is equal to its net ionic charge, we may determine oxidation number of Mn in MnO_4^- ion in the following way.

$$Mn + 4(O) = -1$$
$$(Mn) + 4(-2) = -1$$
$$Mn - 8 = -1$$
$$Mn = +7$$



Example 12.2

Balance the following equation by ion electron method.

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Solution:

The skeleton equation is given as

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Step-1: Transform the molecular equation into ionic form:

$$H^+ + NO_3^- + H_2S \longrightarrow NO + S + H_2O$$

The oxidizing agent is the nitrate ion (NO_3^-) since its nitrogen atom undergoes a decrease in oxidation state. The reducing agent is H_2S since sulphur atom undergoes an increase in oxidation state. H_2S could have been written as sulphide ion (S^{-2}), but H_2S is preferable due to slight degree of ionization.

Step-2: Split the equation into oxidation and reduction half equations.

$NO_3^- \longrightarrow NO$ Reduction (Nitrogen from +5 to +2)

$H_2S \longrightarrow S$ Oxidation (Sulphur from -2 to 0)

Step-3: Since the medium is acidic, oxygen atoms are balanced by adding $2H_2O$ on right hand side and hydrogen atom are balance by $4H^+$ on left hand side in the first partial equation.

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

In the second partial equation two protons are added to the right to balance two hydrogen atoms on the left.

$$H_2S \longrightarrow S + 2H^+$$

Step-4: Balance the charge in the partial equations by adding electrons.

In first partial equation, the oxidation number of nitrogen decreases from +5 to +2, hence 3 electrons are added to the left side.

$$NO_3^- + 4H^+ + 3\bar{e} \longrightarrow NO + 2H_2O$$

In the second partial equation, the oxidation of sulphur increases from -2 to zero hence 2 electron are added to make it zero on the left

$$H_2S \longrightarrow S + 2H^+ + 2\bar{e}^-$$

Step-5: In order to equalize the electrons lost and gain, first partial equation is multiplied by 2 and second by 3.

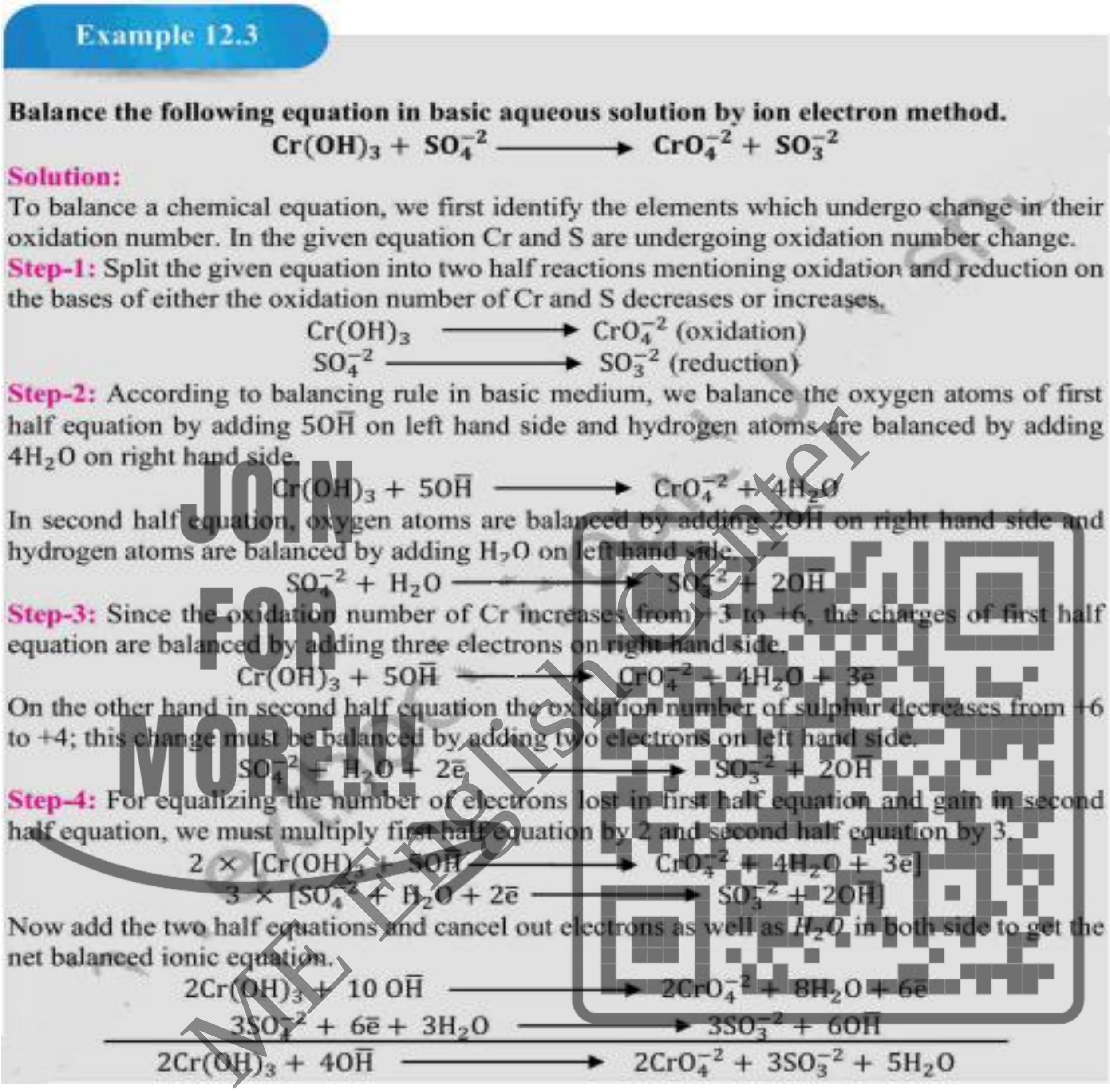
$$2NO_3^- + 8H^+ + 6\bar{e} \longrightarrow 2NO + 4H_2O$$
$$3H_2S \longrightarrow 3S + 6H^+ + 6\bar{e}$$

Step-6: Cancel out the electron and add the partial equations.

$$2NO_3^- + 8H^+ + 6\bar{e} \longrightarrow 2NO + 4H_2O$$
$$3H_2S \longrightarrow 3S + 6H^+ + 6\bar{e}$$
$$\overline{2NO_3^- + 3H_2S + 2H^+ \longrightarrow 2NO + 3S + 4H_2O}$$

This equation may be converted back to molecular form by combining NO_3^- and H^+

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$$



Example 12.3

Balance the following equation in basic aqueous solution by ion electron method.

$$Cr(OH)_3 + SO_4^{-2} \longrightarrow CrO_4^{-2} + SO_3^{-2}$$

Solution:

To balance a chemical equation, we first identify the elements which undergo change in their oxidation number. In the given equation Cr and S are undergoing oxidation number change.

Step-1: Split the given equation into two half reactions mentioning oxidation and reduction on the bases of either the oxidation number of Cr and S decreases or increases.

$$Cr(OH)_3 \longrightarrow CrO_4^{-2} \text{ (oxidation)}$$

$$SO_4^{-2} \longrightarrow SO_3^{-2} \text{ (reduction)}$$

Step-2: According to balancing rule in basic medium, we balance the oxygen atoms of first half equation by adding $5O\bar{H}$ on left hand side and hydrogen atoms are balanced by adding $4H_2O$ on right hand side.

$$Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O$$

In second half equation, oxygen atoms are balanced by adding $2O\bar{H}$ on right hand side and hydrogen atoms are balanced by adding H_2O on left hand side.

$$SO_4^{-2} + H_2O \longrightarrow SO_3^{-2} + 2O\bar{H}$$

Step-3: Since the oxidation number of Cr increases from +3 to +6, the charges of first half equation are balanced by adding three electrons on right hand side.

$$Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O + 3\bar{e}$$

On the other hand in second half equation the oxidation number of sulphur decreases from +6 to +4; this change must be balanced by adding two electrons on left hand side.

$$SO_4^{-2} + H_2O + 2\bar{e} \longrightarrow SO_3^{-2} + 2O\bar{H}$$

Step-4: For equalizing the number of electrons lost in first half equation and gain in second half equation, we must multiply first half equation by 2 and second half equation by 3.

$$2 \times [Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O + 3\bar{e}]$$

$$3 \times [SO_4^{-2} + H_2O + 2\bar{e} \longrightarrow SO_3^{-2} + 2O\bar{H}]$$

Now add the two half equations and cancel out electrons as well as *H_2O* in both side to get the net balanced ionic equation.

$$2Cr(OH)_3 + 10\,O\bar{H} \longrightarrow 2CrO_4^{-2} + 8H_2O + 6\bar{e}$$

$$3SO_4^{-2} + 6\bar{e} + 3H_2O \longrightarrow 3SO_3^{-2} + 6O\bar{H}$$

$$2Cr(OH)_3 + 4O\bar{H} \longrightarrow 2CrO_4^{-2} + 3SO_3^{-2} + 5H_2O$$

Short Questions

1. Define the following:

- **Primary and secondary cell**
- **Oxidizing agent and reducing agent**
- **Redox reactions**
- **Oxidation and reduction**
- **Oxidation number**

Ans)

Primary Cell: In this type of batteries redox reaction takes place in only one direction and cannot be reversed. Thus these batteries cannot be recharged or reused.

Secondary cell: These cells can be recharged by reversing the electricity flow through the cell by utilizing a source of external power supply after every use.

Oxidizing agent: The substance which oxidizes other substances and itself gets reduced in the reaction is called oxidizing agent.

Reducing agent: The substance which reduces other substances and itself gets oxidized in the reaction is called reducing agent.

Redox reaction: Reduction and oxidation reactions, collectively known as redox reactions, are associated with the electrons transfer from one species to another.

Oxidation: It is defined as

Addition of oxygen

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \text{ (Al is oxidized to } Al_2O_3\text{)}$$

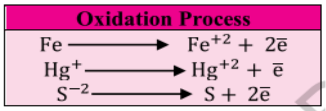
Or

Removal of hydrogen

$$H_2S + Cl_2 \longrightarrow 2HCl + S \text{ (}H_2S\text{ is oxidized to elemental sulphur)}$$

Or

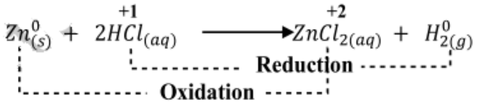
Loss of electrons



Oxidation Process
$Fe \longrightarrow Fe^{+2} + 2\bar{e}$
$Hg^{+} \longrightarrow Hg^{+2} + \bar{e}$
$S^{-2} \longrightarrow S + 2\bar{e}$

Or

Increase in oxidation number



$$Zn^{0}_{(s)} + 2\overset{+1}{H}Cl_{(aq)} \longrightarrow \overset{+2}{Zn}Cl_{2(aq)} + H^{0}_{2(g)}$$

Reduction: It is defined as

Removal of oxygen

$$2CuO \longrightarrow 2Cu + O_2$$ (Copper oxide is reduced to elemental copper)

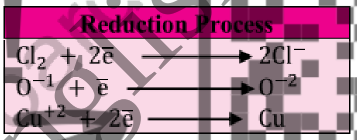
Or

Addition of hydrogen

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$ (Tungsten oxide is reduced to elemental tungsten)

Or

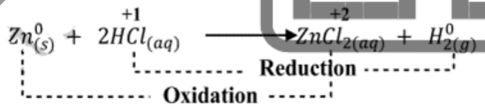
Gain of electrons



Reduction Process
$Cl_2 + 2\bar{e} \longrightarrow 2Cl^-$
$O^{-1} + \bar{e} \longrightarrow O^{-2}$
$Cu^{+2} + 2\bar{e} \longrightarrow Cu$

Or

Decrease in oxidation number



$$Zn^{0}_{(s)} + 2\overset{+1}{H}Cl_{(aq)} \longrightarrow \overset{+2}{Zn}Cl_{2(aq)} + H^{0}_{2(g)}$$

Oxidation Number: Oxidation number is an apparent charge on an atom in a compound or ion. Its value may be positive, negative or zero depending upon charge of combined atoms in the molecule or ion.

2. What is meant by oxidation number? Determine the oxidation number in following.

(i) Cr in H_2CrO_4 **(ii) S in $K_2S_4O_6$**

(iii) Fe in Fe_3O_4 **(iv) Cl in $HClO_4$**

Ans)

Oxidation Number: Oxidation number is an apparent charge on an atom in a compound or ion. Its value may be positive, negative or zero depending upon charge of combined atoms in the molecule or ion.

(i) 2(+1) + Cr + 4(-2) = 0

Cr = +6

(ii) 2(+1) + 4S + 6(-2) = 0

S = +$\frac{5}{2}$

(iii) 3Fe + 4(-2) = 0

Fe = +$\frac{8}{3}$

(iv) (+1) + Cl +4(-2) = 0

Cl = +7

3. Define the term standard electrode potential and hydrogen electrode.

Ans)

Standard Electrode Potential: The electric potential developed on an electrode when it is in equilibrium with 1M solution of its ions at 298K is called standard electrode potential.

Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE) is a primary reference electrode used in electrochemistry to measure the electrode potential of other half-cells in electrochemical cells.

4. In the process of electroplating the item to be plated is made cathode, give reason?

Ans) In electroplating, the item to be plated is made the cathode (negative electrode) because it allows for controlled and precise deposition of the plating material onto the object's surface. This arrangement protects the object from oxidation, promotes better adhesion and bonding of the plated layer, and ensures efficient use of the plating material.

5. What is corrosion? What causes it to form? What can be done to prevent its formation?

Ans)

Corrosion: A spontaneous process in which surface atoms of metals get oxidized (harmful oxides) due to the action of surrounding medium is known as corrosion.

Causes of corrosion: Key factors contributing to corrosion include the presence of oxygen and moisture, the influence of ions, temperature, acidity or alkalinity, and the metal's composition. Environmental conditions and metallurgical factors also play a role.

Prevention against corrosion:

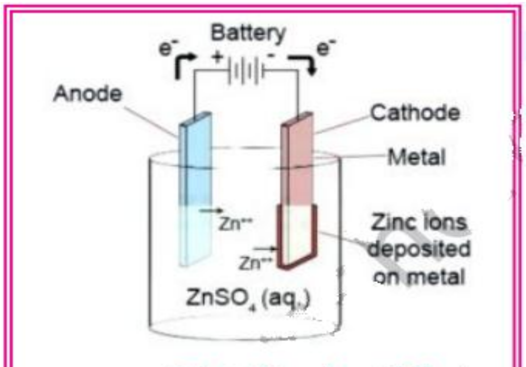
1. Coating: Coating of iron with paint, enamel, grease, oil etc protects iron from corrosion.

2. Electroplating: Electroplating is the coating of one metal on the surface of another by involving electrolysis.

Vegetable oil, food and juice containers are generally tin plated. Tin plating protects iron as long as it remains coated, if scratched then iron exposed to air and starts to get corrosion.

3. Alloying the Iron with other metals: If iron is converted to stainless steel (an alloy of iron) it is protected from corrosion. Stainless steel beside iron contains 8% nickel, 18% chromium and 0.18% carbon.

4. Galvanizing: The process of coating a thin layer of zinc on a metal is known as galvanizing". Since zinc is placed above iron in ECS, it preferably oxidizes and consumes rather than iron and thus protects the iron against corrosion. Galvanizing is carried out either by spraying molten zinc on the surface of iron made material or by dipping the iron sheets into molten zinc.



Galvanizing of metal sheet

6. How can you define an electrochemical series? Give its properties.

Ans)

The Electrochemical Series: A list in which elements are arranged according to their standard electrode potentials is called electrochemical series.

Properties of Electrochemical Series: Key properties of the electrochemical series include:

1. It arranges substances by their tendency to gain or lose electrons in redox reactions.
2. The reference point is the standard hydrogen electrode (SHE) with a standard potential of 0.00 V.
3. Elements at the top have a strong tendency to undergo reduction (act as reducing agents), while those at the bottom tend to undergo oxidation (act as oxidizing agents).
4. It has practical applications in designing electrochemical cells, studying corrosion, and assessing redox reactions.

Descriptive Questions

1. (a) What is meant by electrode potential and standard Hydrogen electrode (SHE).

Ans)

Electrode Potential:

Definition: The electric potential developed on an electrode when it is in equilibrium with its ions is called electrode potential.

Representation: It is represented by letter "E".

Types: Electrode potential is of two types

1. Oxidation potential
2. Reduction potential

Oxidation potential: The tendency of a substance to be oxidized is called its oxidation potential.

Reduction potential: The tendency of a substance to be reduced is its called reduction potential.

Standard Electrode Potential:

Definition: The electric potential developed on an electrode when it is in equilibrium with 1M solution of its ions at 298K is called standard electrode potential.

Representation: It is represented by letter “E^o”.

Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE) is a primary reference electrode used in electrochemistry to measure the electrode potential of other half-cells in electrochemical cells.

Standard Hydrogen Electrode i.e. SHE consists of a platinum foil, which is coated electrolytically with finely divided platinum black and suspended in 1M HCI soln. It is enclosed in a glass tube as shown in figure. Pure hydrogen gas at 1 atm is continually supplied to it. Electrode potential of hydrogen electrode is arbitrarily chosen as zero.

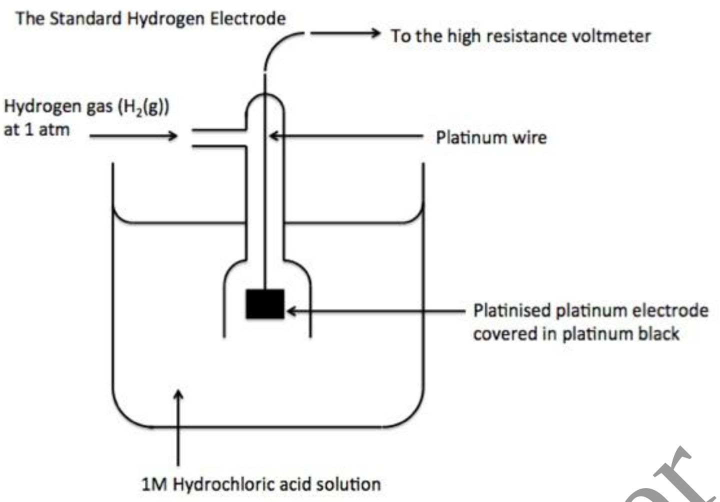
$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^o_{Red} = 0.000\ V$$

$$H_2 \longrightarrow 2H^+ + 2e^- \qquad E^o_{ox} = 0.000\ V$$

Although SHE is primary reference electrode but it is inconvenient to use because

1. It is difficult to maintain the cone of HCI solution at 1M during use.
2. It is difficult to maintain the pressure of H_2 gas at 1 atm during use.
3. Platinum get contaminated during use.

Hence secondary reference electrodes are used for determination of electrode potentials instead of SHE. However the electrode potentials of secondary reference electrodes are measured by SHE.



Standard Hydrogen Electrode (SHE)

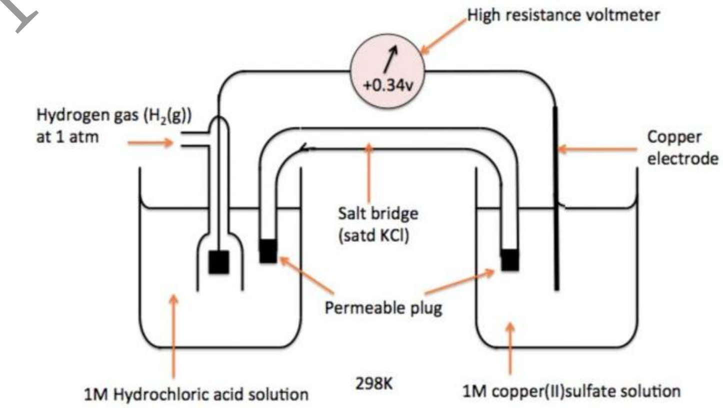
(b) Describe how the electrode potential of copper is determined.

Ans)

Measure of electrode potential of copper: Similarly to measure the electrode potential of copper electrode, a galvanic or voltaic cell is established between copper electrode and standard hydrogen electrode. Reading on volt meter is taken under standard conditions, Volt meter reads 0.34V. Direction of current is from hydrogen electrode to copper electrode, it means reduction occurred at copper electrode so its reduction potential is higher than that of hydrogen electrode by 0.34 volt. Thus reduction potential of copper electrode is +0.34 V while its oxidation potential will be-0.34 V.

$$E^o_{Cu+2/Cu} = +0.34\ V$$

$$E^o_{Cu/Cu+2} = -0.34\ V$$

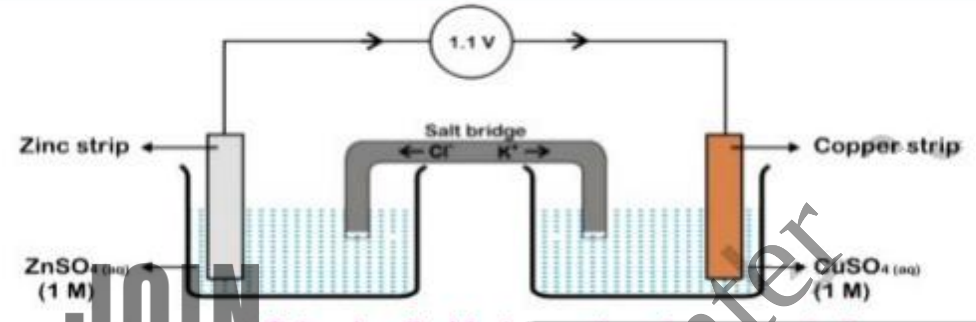


Measurement of electrode potential of Copper

2. Sketch a copper-zinc Galvanic cell, write the cell reaction and show the direction of electron flow.

Ans)

Sketch of a copper-zinc Galvanic cell:



A Galvanic cell with zinc anode and copper cathode

Reaction: The two half cell reactions and the net reaction can be written as

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at zinc half cell)}$$
$$Cu^{+2}_{(s)} + 2\bar{e} \longrightarrow Cu_{(aq)} \text{ (Reduction at copper half cell)}$$
$$\overline{Zn_{(s)} + Cu^{+2}_{(s)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(aq)} \text{ (Net cell reaction)}}$$

Galvanic cells are conveniently express in some short hand notations. For example Zinc-copper cell may be written as.

$$\underset{\text{(anode)}}{Zn_{(s)}}\,\big|\,Zn^{+2}_{(aq)}\,\underset{\text{salt bridge}}{||}\,Cu^{+2}_{(aq)}\,\big|\,\underset{\text{(cathode)}}{Cu_{(s)}}$$

Here single vertical line specifies the phase boundary between electrode and electrolytic solution where as double vertical lines indicate salt bridge.

Direction of electron flow: The direction of electron flow is from zinc to copper electrode as shown in figure above.

3. What is the difference between a primary cell and secondary cell. Sketch a diagram of dry cell and explain its working.

Ans)

Characteristic	Primary Cells	Secondary Cells
Also Known As	Non-rechargeable cells	Rechargeable cells
Reusability	Single-use	Reusable
Lifespan	Limited (usually one-time use)	Reusable, longer lifespan
Capacity Maintenance	Capacity degrades over time	Capacity can be maintained

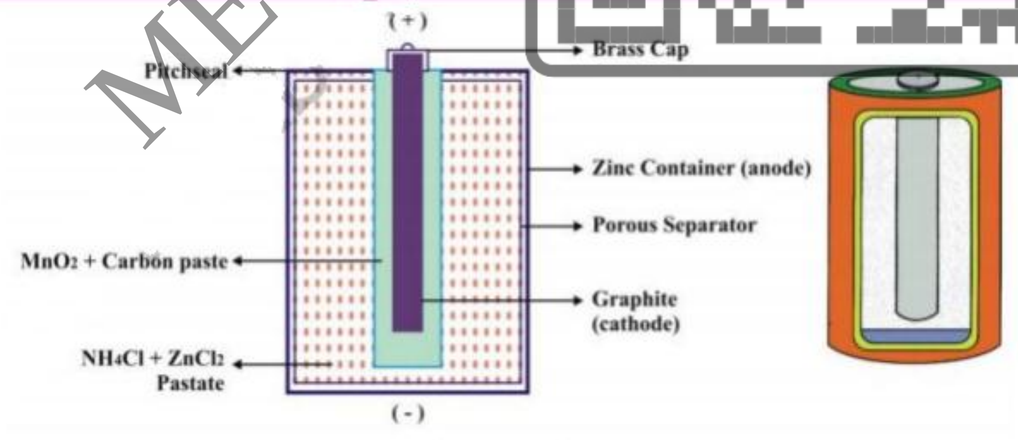
Dry Cell:

Working: When the cell starts working Zn anode oxidizes to Zn^{+2} ions whereas at graphite cathode Mn^{+4} ions reduces to Mn^{+3} ions.

Reaction:

$$Zn \longrightarrow Zn^{+2} + 2\bar{e} \text{ (anode)}$$
$$2NH_4^+ + 2MnO_2 + 2\bar{e} \longrightarrow Mn_2O_3 + 2NH_3 + H_2O \text{ (cathode)}$$

The electrons generated at anode flow out to the external circuit. This cell produces 1.5 volt electric current and become dead after complete utilizing zinc electrode.



Structure of common dry cell

4. Balance the following equations by ion electron method.

(i) $Cr_2O_7^{-2} + I_2 \longrightarrow Cr^{+3} + IO_3^-$ **(acidic medium)**

Solution:

Step # 1: Split the equations into two parts

$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$

$I_2 \longrightarrow IO_3^-$

Step # 2: Balance all the elements except oxygen and hydrogen

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$

$I_2 \longrightarrow 2IO_3^-$

Step # 3: Balance oxygen by adding H_2O

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$6H_2O + I_2 \longrightarrow 2IO_3^-$

Step # 4: Balance hydrogen by adding H^+

$14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$6H_2O + I_2 \longrightarrow 2IO_3^- + 12H^+$

Step # 5: Balance the charges by adding e^-

$6e^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ …..(i)

$6H_2O + I_2 \longrightarrow 2IO_3^- + 12H^+ + 10e^-$ …….(ii)

Step # 6: Cancel out the electrons

Multiplying eqn (i) by 5 and eqn (ii) by 3

$\cancel{30e^-} + 70H^+ + 5Cr_2O_7^{-2} \longrightarrow 10Cr^{+3} + 35H_2O$

$18H_2O + 3I_2 \longrightarrow 6IO_3^- + 36H^+ + \cancel{30e^-}$

$\mathbf{5Cr_2O_7^{-2} + 3I_2 + 34H^+ \longrightarrow 10Cr^{+3} + 6IO_3^- + 17H_2O}$

(ii) $MnO_4^- + SO_3^{-2} \longrightarrow Mn^{+2} + SO_4^{-2}$ (basic medium)

Solution:

Step # 1: Split the equations into two parts

$MnO_4^- \longrightarrow Mn^{+2}$

$SO_3^{-2} \longrightarrow SO_4^{-2}$

Step # 2: Balance all the elements except oxygen and hydrogen

They are already balance

Step # 3: Balance oxygen by adding H_2O

$MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

$H_2O + SO_3^{-2} \longrightarrow SO_4^{-2}$

Step # 4: Balance hydrogen by adding H^+

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

$H_2O + SO_3^{-2} \longrightarrow SO_4^{-2} + 2H^+$

Step # 5: Add OH^- on both sides according to H^+

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

$2OH^- + H_2O + SO_3^{-2} \longrightarrow SO_4^{-2} + 2H^+ + 2OH^-$

$8H_2O + MnO_4^- \longrightarrow Mn^{+2} + 4H_2O + 8OH^-$

$2OH^- + H_2O + SO_3^{-2} \longrightarrow SO_4^{-2} + 2H_2O$

Step # 6: Balance the charges by adding e^-

$5e^- + 4H_2O + MnO_4^- \longrightarrow Mn^{+2} + 8OH^-$ ……(i)

$2OH^- + SO_3^{-2} \longrightarrow SO_4^{-2} + H_2O + 2e^-$ …….(ii)

Step # 7: Cancel out the electrons

Multiplying eqn (i) by 2 and eqn (ii) by 5

$\cancel{10e^-} + 8H_2O + 2MnO_4^- \longrightarrow 2Mn^{+2} + 16OH^-$

$10\,OH^- + 5SO_3^{-2} \longrightarrow 5SO_4^{-2} + 5H_2O + \cancel{10e^-}$

$2MnO_4^- + 5SO_3^{-2} + 3H_2O \longrightarrow 2Mn^{+2} + 5SO_4^{-2} + 6OH^-$

(iii) $MnO_4^- + Cl^- \longrightarrow Mn^{+2} + Cl_2$ (acidic medium)

Solution:

Step # 1: Split the equations into two parts

$MnO_4^- \longrightarrow Mn^{+2}$

$Cl^- \longrightarrow Cl_2$

Step # 2: Balance all the elements except oxygen and hydrogen

$MnO_4^- \longrightarrow Mn^{+2}$

$2Cl^- \longrightarrow Cl_2$

Step # 3: Balance oxygen by adding H_2O

$MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

$2Cl^- \longrightarrow Cl_2$

Step # 4: Balance hydrogen by adding H^+

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

$2Cl^- \longrightarrow Cl_2$

Step # 5: Balance the charges by adding e^-

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

$2Cl^- \longrightarrow Cl_2 + 2e^-$ ......(ii)

Step # 6: Cancel out the electrons

Multiplying eqn (i) by 2 and eqn (ii) by 5

$\cancel{10e-} + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{+2} + 8H_2O$

$10Cl^- \longrightarrow 5Cl_2 + \cancel{10e^-}$

$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{+2} + 5Cl_2 + 8H_2O$

(iv) $Cl_2 + OH^- \longrightarrow Cl- + ClO_3^- + H_2O$ (basic medium)

Solution:

Step # 1: Split the equations into two parts

$Cl_2 \longrightarrow Cl^-$

$Cl_2 \longrightarrow ClO_3^-$

Step # 2: Balance all the elements except oxygen and hydrogen

$Cl_2 \longrightarrow 2Cl^-$

$Cl_2 \longrightarrow 2ClO_3^-$

Step # 3: Balance oxygen by adding H_2O

$Cl_2 \longrightarrow 2Cl^-$

$6H_2O + Cl_2 \longrightarrow 2ClO_3^-$

Step # 4: Balance hydrogen by adding H^+

$Cl_2 \longrightarrow 2Cl^-$

$6H_2O + Cl_2 \longrightarrow 2ClO_3^- + 12H^+$

Step # 5: Add OH^- on both sides according to H^+

$Cl_2 \longrightarrow 2Cl^-$

$12OH^- + 6H_2O + Cl_2 \longrightarrow 2ClO_3^- + 12H^+ + 12OH^-$

$Cl_2 \longrightarrow 2Cl^-$

$12OH^- + 6H_2O + Cl_2 \longrightarrow 2ClO_3^- + 12H_2O$

Step # 6: Balance the charges by adding e^-

$2e^- + Cl_2 \longrightarrow 2Cl^-$ ….(i)

$12OH^- + Cl_2 \longrightarrow 2ClO_3^- + 6H_2O + 10e^-$

Step # 7: Cancel out the electrons

Multiplying eqn (i) by 5

$\cancel{10e^-} + 5Cl_2 \longrightarrow 10Cl^-$

$12OH^- + Cl_2 \longrightarrow 2ClO_3^- + 6H_2O + \cancel{10e^-}$

$\mathbf{6\,Cl_2 + 12OH^- \longrightarrow 10Cl^- + 2ClO_3^- + 6H_2O}$

(v) $MnO_4^- + C_2O_4^{-2} + H^+ \longrightarrow Mn^{+2} + CO_2 + H_2O$ (acidic medium)

Solution:

Step # 1: Split the equations into two parts

$MnO_4^- \longrightarrow Mn^{+2}$

$C_2O_4^{-2} \longrightarrow CO_2$

Step # 2: Balance all the elements except oxygen and hydrogen

$MnO_4^- \longrightarrow Mn^{+2}$

$C_2O_4^{-2} \longrightarrow 2CO_2$

Step # 3: Balance oxygen by adding H_2O

$MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

$C_2O_4^{-2} \longrightarrow 2CO_2$

Step # 4: Balance hydrogen by adding H^+

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

$C_2O_4^{-2} \longrightarrow 2CO_2$

Step # 5: Balance the charges by adding e^-

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

$C_2O_4^{-2} \longrightarrow 2CO_2 + 2e^-$…..(ii)

Step # 6: Cancel out the electrons

Multiplying eqn (i) by 2

$\cancel{10e^-} + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{+2} + 8H_2O$

$5C_2O_4^{-2} \longrightarrow 10CO_2 + \cancel{10e^-}$

$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$

(vi) $Fe^{+2} + Cr_2O_7^{-2} + H^+ \longrightarrow Fe^{+3} + Cr^{+3} + H_2O$ (acidic medium)

Solution:

Step # 1: Split the equations into two parts

$Fe^{+2} \longrightarrow Fe^{+3}$

$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$

Step # 2: Balance all the elements except oxygen and hydrogen

$Fe^{+2} \longrightarrow Fe^{+3}$

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$

Step # 3: Balance oxygen by adding H_2O

$Fe^{+2} \longrightarrow Fe^{+3}$

$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

Step # 4: Balance hydrogen by adding H^+

$Fe^{+2} \longrightarrow Fe^{+3}$

$14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

Step # 5: Balance the charges by adding e^-

$Fe^{+2} \longrightarrow Fe^{+3} + 1e^-$ …..(i)

$6e^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$…..(ii)

Step # 6: Cancel out the electrons

Multiplying eqn (i) by 6

$6\,Fe^{+2} \longrightarrow 6Fe^{+3} + 6e^-$

$6e^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$6\,Fe^{+2} + Cr_2O_7^{-2} + 14H^+ \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O$