XI – CHEMISTRY

Name :

Class : **Sec** :

School :

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UNIT 1 BASIC CONCEPTS OF CHEMISTRY AND CHEMICAL CALCULATIONS

I. Answer the following.

26. Define relative atomic mass.

On the basis of carbon, the relative atomic mass of element is defined as the ratio of mass of one atom of the element to the mass of l/12th mass of one atom of Carbon – 12.

$$\text{Relative atomic mass} = \frac{\text{Mass of one atom of the element}}{\text{Mass of 1/12}^{th} \text{ mass of one atom of Carbon-12}}$$

27. What do you understand by the term mole?

The mole is defined as the amount of a substance which contains 6.023×10^{23} particles such as atoms, molecules or ions. It is represented by the symbol

28. Define equivalent mass.

The equivalent mass of an element is the number of parts of the mass of an element which combines with or displaces 1.008 parts of hydrogen or 8 parts of oxygen or 35.5 parts of chlorine.

29. What do you understand by the term oxidation number?

Oxidation number refers to the number of charges an atom would have in a molecule or an ionic compound, if electrons were transferred completely. The oxidation numbers reflect the number of electrons "transferred".

30. Distinguish between oxidation and reduction.

Oxidation	Reduction
• According to the classical concept, oxidation is a process of addition of oxygen or removal of hydrogen. • Removal of hydrogen $2H_2S + O_2 \rightarrow H_2O + 2S$ Addition of oxygen $C + O_2 \rightarrow CO_2$ • According to the electronic concept, loss of electrons is called oxidation reaction. $Ca \rightarrow Ca^{2+} + 2e^-$ • During oxidation, oxidation number increases. • Dining oxidation, reducing agent gets oxidised.	• Reduction is a process of removal of oxygen or addition of hydrogen. • Addition of hydrogen $Ca + H_2 \rightarrow CaH_2$ Removal of oxygen $Zn\,O + C \rightarrow Zn + CO$ • According to the electronic concept, gain of electrons is called reduction reaction. $Zn^{2+} + 2e^- \rightarrow Zn$ • During reduction, oxidation number decreases. • During reduction, oxidising agent gets reduced.

31. Calculate the molar mass of the following compounds.

1. urea [$CO(NH_2)_2$]   2. acetone [CH_3COCH_3] 3. boric acid [H_3BO_3] 4. sulphuric acid [H_2SO_4]

1. urea [$CO(NH_2)_2$]

Atomic mass of C =12
Atomic mass of O =16
Atomic mass of 2(N) = 28
Atomic mass of 4(H) = 4
∴ Molar mass of Urea = 60

2. Acetone [CH_3COCH_3]

Atomic mass of 3(C) = 36
Atomic mass of 1(0) = 16
Atomic mass of 6(H) = 6
∴ Molar mass of Acetone = 58

3. Boric acid [H_3BO_3]

Atomic mass of B = 10
Atomic mass of 3(H) = 3
Atomic mass of 3(O) = 48
∴ Molar mass of Boric acid = 61

4. Sulphuric acid $_2$[H_2SO_4]

Atomic mass of 2(H) = 2
Atomic mass of 1(S) = 32
Atomic mass of 4(O) = 64
∴ Molar mass of Sulphuric acid = 98

32. The density of carbon dioxide is equal to 1.977 kg m^{-3} at 273 K and 1 atm pressure. Calculate the molar mass of CO_2

Molecular mass = Density x Molar volume
Molar volume of CO_2 = 2.24×10^{-2} m^3
Density of CO_2 = 1.977 kg m^{-3}
Molecular mass of CO_2 = 1.977×10^3 gm^{-3} x 2.24×10^{-2} m^3
= $1.977 \times 10^{-1} \times 2.24 = 44$ g

33. Which contains the greatest number of moles of oxygen atoms?

  i.   1 mol of ethanol
 ii.   1 mol of formic acid
iii.   1 mol of H_2O

(i) 1 mol of ethanol

C_2H_5OH (ethanol) – Molar mass = 24 + 6 + 16 = 46
46 g of ethanol contains $1 \times 6.023 \times 10^{23}$ number of oxygen atoms.

(ii) 1 mol of formic acid.

HCOOH (formic acid) – Molar mass = 2+12 + 32 = 46
46 g of HCOOH contains $2 \times 6.023 \times 10^{23}$ number of oxygen atoms.

(iii) 1 mol of H_2O

H_2O (water) – Molar mass = 2 + 16 = 18

18 g of water contains $1 \times 6.023 \times 10^{23}$ number of oxygen atoms.

∴ 1 mole of formic acid contains the greatest number of oxygen atoms.

34. Calculate the average atomic mass of naturally occurring magnesium using the following data

Isotope	Isotopic atomic mass	Abundance (%)
Mg^{24}	23.99	78.99
Mg^{26}	24.99	10
Mg^{25}	25.98	11.01

Isotopes of Mg.

Atomic mass = Mg^{24} = 23.99 x $\frac{78}{100}$3.99100 = 18.95

Atomic mass = Mg^{26} = 24.99 x 10100 = 2.499

Atomic mass = Mg^{25} = 25.98 x 11.01100 = 2.860

Average Atomic mass = 24.309

Average atomic mass of Mg = 24.309

35. In a reaction $x + y + z_2 \rightarrow xyz_2$, identify the limiting reagent if any, in the following reaction mixtures.

(a) 200 atoms of x + 200 atoms of y + 50 molecules of z_2

(b) 1 mol of x + 1 mol of y + 3 mol of z_2

(c) 50 atoms of x + 25 atoms of y + 50 molecules of z_2

(d) 2.5 mol of x + 5 mol of y + 5 mol of z_2

Answer:

(a) 200 atoms of x + 200 atoms of y + 50 molecules of z_2 According to the reaction, 1 atom of x reacts with one atom of y and one molecule of z to give product. In the case (a) 200 atoms of x, 200 atoms of y react with 50 molecules of z_2 (4 part) i.e. 50 molecules of z_2 react with 50 atoms of x and 50 atoms of y. Hence z is the limiting reagent.

(b) 1 mol of x + 1 mol of y + 3 mol of z_2

According to the equation 1 mole of z_2 only react with one mole of x and one mole of y. If 3 moles of z_2 are there, z is limiting reagent.

(c) 50 atoms of x + 25 atoms of y + 50 molecules of z_2

25 atoms of y react with 25 atoms of x and 25 molecules of z_2. So y is the limiting reagent.

(d) 2.5 mol of x + 5 mol of y + 5 mol of z_2

2.5 mol of x react with 2.5 mole of y and 2.5 mole of z_2. So x is the limiting reagent.

36. Mass of one atom of an element is 6.645×10^{-23} g. How many moles of element are there in 0.320 kg?

Mass of one atom of an element = 6.645×10^{-23} g = Atomic mass.

Mass of given element = 0.320 kg

Number of moles =

Atomic mass

$$Number\ of\ moles = \frac{Mass}{Atomic\ mass}$$
$$= \frac{0.320 \times 1000\ g}{6.645 \times 10^{-23}\ g}$$
$$= \frac{320 \times 10^{23}}{6.645}$$
$$= 48.156 \times 10^{23}$$
$$= 4.8156 \times 10^{24}\ moles.$$

37. What is the difference between molecular mass and molar mass? Calculate the molecular mass and molar mass for carbon monoxide.

Molecular mass	Molar mass:
- Relative molecular mass is defined as the ratio of the mass of the molecule to the unified atomic mass unit. - It can be calculated by adding the relative atomic masses of its constituent atoms. - For carbon monoxide (CO) Molecular mass = Atomic mass of carbon + Atomic mass of oxygen 12 + 16 = 28 u.	- It is defined as the mass of one mole of a substance. - The molar mass of a compound is equal to the sum of the relative atomic masses of its constituent expressed in g mol^{-1}. - For carbon monoxide (CO) 12 + 16 = 28 g mol^{-1} Both molecular mass and molar mass are numerically same but the units are different.

38. What is the empirical formula of the following?
   1. **Fructose ($C_6H_{12}O_6$) found in honey**
   2. **Caffeine ($C_8H_{10}N_4O_2$) a substance found in tea and coffee.**

1. Fructose ($C_6H_{12}O_6$)

Empirical formula is the simplest formula. So it is divided by 6 and so empirical formula is CH_2O.

2. Caffeine ($C_8H_{10}N_4O_2$)

Simplified formula = $\frac{molecular formula}{2}$

Empirical formula = $C_4H_5N_2O$.

39. The reaction between aluminium and ferric oxide can generate temperatures up to 3273 K and is used in welding metals. (Atomic mass of AC = 21 u Atomic mass of 0 = 16 u) 2Al + Fe$_2$O$_2$ → Al$_2$O$_3$ + 2Fe; If, in this process, 324 g of aluminium is allowed to react with 1.12 kg of ferric oxide.

1. **Calculate the mass of Al_2O_3 formed.**
2. **How much of the excess reagent is left at the end of the reaction?**

(i) $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$
        54g   160g   102g   112g
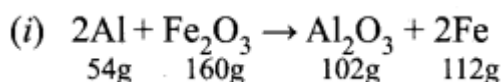
1. As per balanced equation 54 g A1 is required for 112 g of iron and 102 g of Al_2O_3.
54 g of Al gives 102 g of Al_2O_3.
∴ 324 g of Al will give $\frac{102}{54}$ x 324 = 612 g of Al_2O_3.
2. 54 g of Al requires 160 g of Fe_2O_3 for welding reaction.
∴ 324 g of Al will require $\frac{160}{54}$ x 324 = 960 g of Fe_2O_3.
∴ Excess Fe_2O_3 – Un reacted Fe_2O_3 = 1120 – 960 = 160 g
160 g of excess reagent is left at the end of the reaction.

40. How many moles of ethane is required to produce 44 g of CO_2 (g) after combustion.

$C_2H_6 + 3\frac{1}{2} O_2 \rightarrow 2CO_2 + 3H_2O$
Ethane   Carbon dioxide
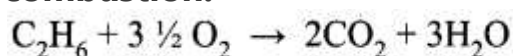
1 mole of ethane $\xrightarrow{\text{Combustion}}$ 2 moles of CO_2
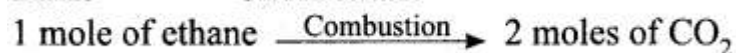
∴ 44g of CO_2 = I mole of CO_2
2 moles of CO_2 is produced by 1 mole of ethane.
∴ 1 mole of CO_2 will be produced by = ?
∴ To produce 1 mole of CO_2, the required mole of ethane is = $\frac{1}{2}$ x 1 = 0.5 mole of ethane.

41. Hydrogen peroxide is an oxidizing agent. It dioxides ferrous ion to ferric ion and reduced itself to water. Write a balanced equation.

H_2O_2 – Oxidizing agent
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + H_2O$ (Acetic medium)
Ferrous ion is oxidized by H_2O_2 to Ferric ion.
The balanced equation is $Fe^{2+} \rightarrow Fe^{3+} + e^- \times 2$
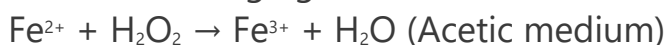
$H_2O_2 + 2H^+ + 2\cancel{e^-} \rightarrow 2H_2O$
$2Fe^{2+} \rightarrow 2Fe^{3+} + 2\cancel{e^-}$
$H_2O_2 + 2H^+ \rightarrow 2H_2O$
$\overline{}$
$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$
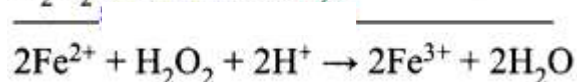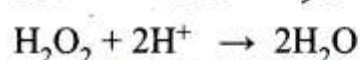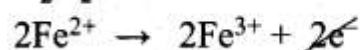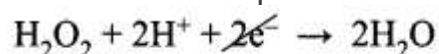
42. Calculate the empirical and molecular formula of a compound containing 76.6% carbon, 6.38 % hydrogen and rest oxygen its vapour density is 47.

Elements	Percentage	Atomic mass	Relative No. of atoms	Simple ratio of atoms	Simplest whole number ratio
Carbon (C)	76.6%	12	$\frac{76.6}{12} = 6.38$	$\frac{6.38}{1.063} = 6$	6
Hydrogen (H)	6.38%	1	$\frac{6.38}{1} = 6.38$	$\frac{6.38}{1.063} = 6$	6
Oxygen (O)	17.02%	16	$\frac{17.02}{16} = 1.063$	$\frac{1.063}{1.063} = 1$	1

Empirical formula = C_6H_6O

Vapour density 47

∴ Molecular mass = 2 x vapor density = 2 x 47 = 94

Molecular formula Empirical formula x n

Molecular mass x n

$$n = \frac{Molecular\ mass}{Empirical\ formula\ mass} = \frac{94}{94} = 1$$

∴ Molecular formula = C_6H_6O

43. A Compound on analysis gave Na = 14.31% S = 9.97% H = 6.22% and O = 69.5% calculate the molecular formula of the compound if all the hydrogen in the compound is present in combination with oxygen as water of crystallization, (molecular mass of the compound is 322).

Element	Percentage	Atomic mass	Relative No. of atoms	Simple ratio of atoms	Simplest whole number ratio
Na	14.31%	23	$\frac{14.31}{23} = 0.622$	$\frac{0.622}{0.311} = 2$	2
S	9.97%	32	$\frac{9.97}{32} = 0.311$	$\frac{0.311}{0.311} = 1$	1
H	6.22%	1	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.311} = 20$	20
O	69.5%	16	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.311} = 13.96 = 14$	14

All H combines with 10 oxygen atoms to form as $10H_2O$.

So the empirical formula is $Na_2SO_4 .10H_2 O$

Empirical formula mass = (23 x 2) + (32 x 1) + (16 x 4) + (10 x 18)

= 46 + 32 + 64 + 180 = 322

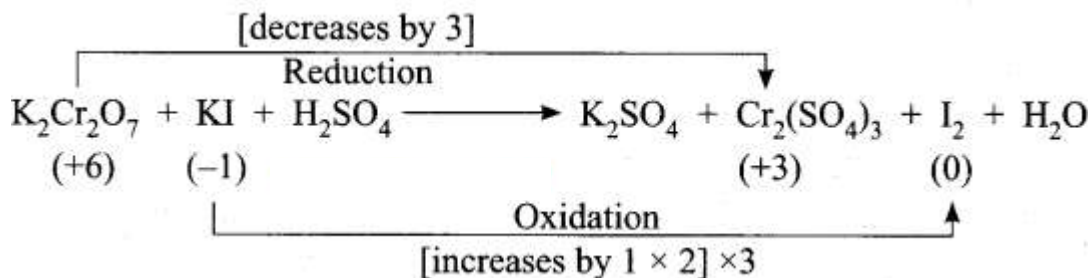$$n = \frac{Molecular\ mass}{Empirical\ formula\ mass} = \frac{322}{322} = 1$$

Molecular formula = $Na_2SO_4. 10H_2O$

44. Balance the following equations by oxidation number method

1. $K_2Cr_2O_7 + KI + H_2SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$
2. $KMnO_4 + Na_2SO_3 \rightarrow MnO_2 + Na_2SO_4 + KOH$
3. $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$
4. $H_2C_2O_4 + KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$

1. $K_2Cr_2O_7 + KI + H_2SO_2 \rightarrow K_2SO_2 + Cr_2(SO_4)_3 + I_2 + H_2O$

Step – 1.

Step – 2

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

Step – 3

To balance other atoms

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

Step – 4

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

2. $KMnO_4 + Na_2SO_3 \rightarrow MnO_2 + Na_2SO_4 + KOH$ (Alkaline medium)

Step – 1

Step – 2

$2KMnO_4 + 3Na_2SO_3 \rightarrow 2MnO_2 + 3Na_2SO_4 + KOH$
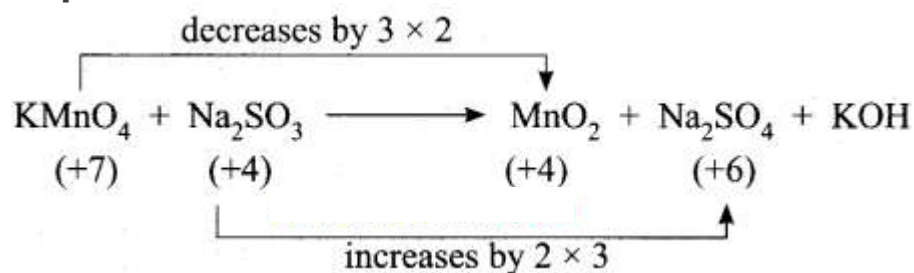
Step – 3

balancing potassium, KOH is multiplied by 2

$2KMnO_4 + 3Na_2SO_3 \rightarrow 2MnO_2 + 3Na_2SO_4 + KOH$

Step – 4

To balance H atom, H_2O is added on reactant side.

$2KMnO_4 + 3Na_2SO_3 + H_2O \rightarrow 2MnO_2 + 3Na_2SO_4 + KOH$

3. Cu + HNO₃ → Cu(NO₃)₂ + NO₂ + H₂O

Step – 1

Step – 2

$Cu + HNO_3 → Cu(NO_3)_2 + NO_2 + H_2O$
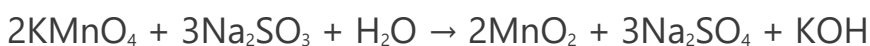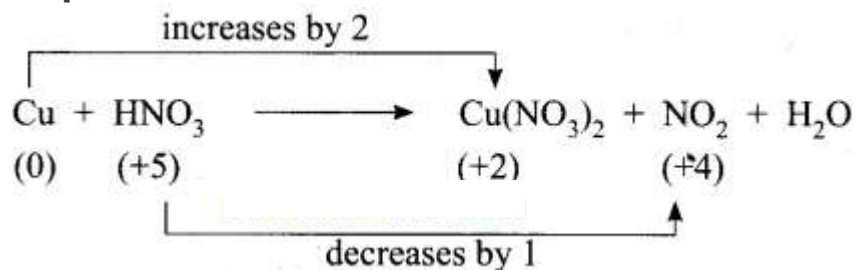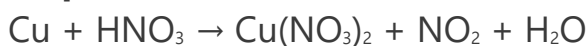
Step – 3

To balance Nitrogen, 2HNO₃ is multiplied by 2 and NO₂ is multiplied by 2

$Cu + 4HNO_3 → Cu(NO_3)_2 + 2NO_2 + H_2O$

Step 4.

To balance oxygen, H₂O is multiplied by 2

$Cu + 4HNO_3 → Cu(NO_3)_2 + 2NO_2 + 2H_2O$

4. H₂C₂O₄ + KMnO₄ + H₂SO₄ → K₂SO₄ + MnSO₄ + CO₂ + H₂O

Step – 1

Step – 2

$5 H_2C_2O_4 + KMnO_4 + H_2SO_4 → K_2SO_4 + MnSO_4 + 10 CO_2 + H_2O$
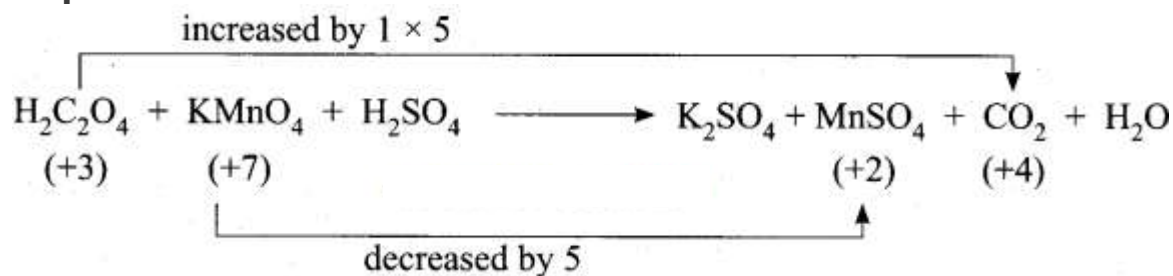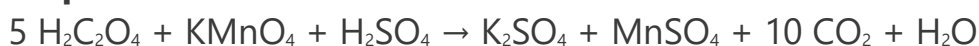
Step – 3

To balance K, KMnO₄ and MnSO₄ are multiplied by 2

$5 H_2C_2O_4 + 2KMnO_4 + H_2SO_4 → K_2SO_4 + 2MnSO_4 + 10 CO_2 + H_2O$

Step – 4

To balance O and H, H₂O and H₂SO₄ are multiplied by 3 and 6.

$5 H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 → K_2SO_4 + 2MnSO_4 + 10 CO_2 + 8H_2O$
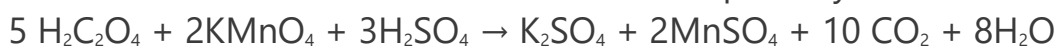
45. Balance the following equations by ion electron method.
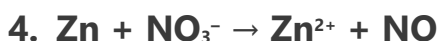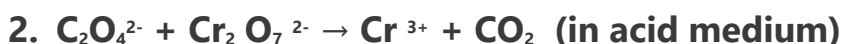
1. $KMnO_4 + SnCl_2 + HCl → MnCl_2 + SnCl_4 + H_2O + KCl$
2. $C_2O_4^{2-} + Cr_2O_7^{2-} → Cr^{3+} + CO_2$ **(in acid medium)**
3. $Na_2S_2O_3 + I_2 → Na_2S_4O_6 + NaI$ **(in acid medium)**
4. $Zn + NO_3^- → Zn^{2+} + NO$

1. $KMnO_4 + SnCl_2 + HCl \rightarrow MnCl_3 + SnCl_3 + H_2O + KCl$

Oxidation half reaction: (loss of electrons)

$$\overset{+2}{SnCl_2} \rightarrow \overset{+4}{SnCl_4} + 2e^- \qquad \ldots\ldots\ldots(1)$$

Reduction half reaction: (gain of electrons)

$$\overset{+7}{KMnO_4} + 5e^- \rightarrow \overset{+2}{MnCl_2} \qquad \ldots\ldots\ldots(2)$$
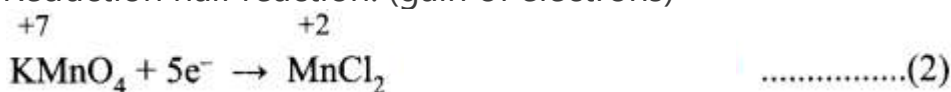
Add H_2O to balance oxygen atoms.

$$KMnO_4 + 5e^- \rightarrow \overset{+2}{MnCl_2} + 4H_2O \qquad \ldots\ldots\ldots(3)$$
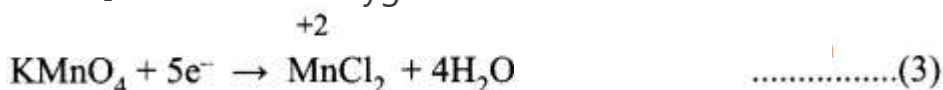
Add HCl to balance hydrogen atoms

$KMnO_4 + 5e_- + 8HCl \rightarrow MnCl_2 + 4H_2O \ldots\ldots(4)$
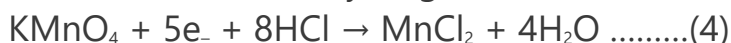
To equalize the number of electrons equation (1) x 5 and equation (2) x 2
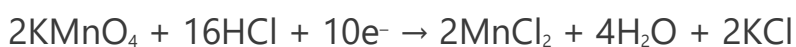
$5SnCl_2 \rightarrow 5SnCl_4 + 10e^-$

$2KMnO_4 + 16HCl + 10e^- \rightarrow 2MnCl_2 + 4H_2O + 2KCl$

$2KMnO_4 + 5SnCl_2 + 16HCl \rightarrow 5SnCl_4 + 2MnCl_2 + 4H_2O + 2KCl$

2. $C_2O_4^{2-} + Cr_2O_7^{2-} \rightarrow Cr^{3+} + CO_2$ (in acid medium)

Oxidation half reaction:

$$\underset{(+3)}{C_2O_4^{2-}} \rightarrow \underset{(+4)}{2CO_2} + 2e^- \qquad \ldots\ldots\ldots(1)$$

Reduction half reaction:

$$\underset{(+6)}{Cr_2O_7^{2-}} + 6e^- \rightarrow 2Cr^{3+} \qquad \ldots\ldots\ldots(2)$$
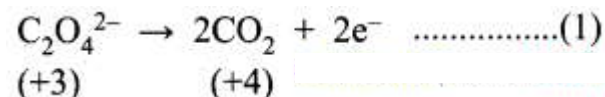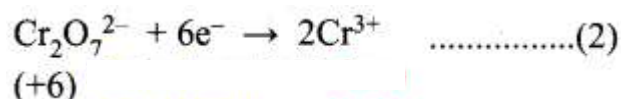
To balance oxygen atoms, H_2O is added on RHS of equation (2)

$Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7\,H_2O \ldots\ldots\ldots(3)$
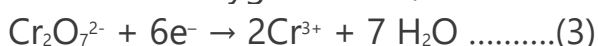
To balance Hydrogen atoms, H^+ is added on LHS of equation (1)

$C_2O_4^{2-} + 14H^+ \rightarrow 2CO_2 + 2e^- \ldots\ldots(4)$

To equalize the number of electrons gained and lost, multiply the equation (4) x 3.
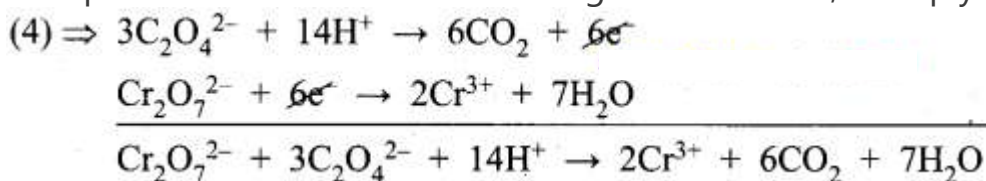
$$(4) \Rightarrow 3C_2O_4^{2-} + 14H^+ \rightarrow 6CO_2 + \cancel{6e^-}$$
$$\underline{Cr_2O_7^{2-} + \cancel{6e^-} \rightarrow 2Cr^{3+} + 7H_2O}$$
$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$$

3. $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$ (in acid medium)

Oxidation half reaction: (Loss of electron)

$Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2e^{2-} \ldots\ldots(1)$

Reduction half reaction: (Gain of electron)

$I_2 + 2e^{2-} \rightarrow 2NaI \ldots\ldots\ldots(2)$

Adding (1) and (2)

$$Na_2S_2O_3 \rightarrow Na_2S_4O_6 + \cancel{2e}$$
$$I_2 + \cancel{2e} \rightarrow 2NaI$$
$$\overline{Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI}$$

To balance oxygen,

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_2O_2 + 2NaI$
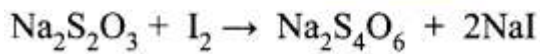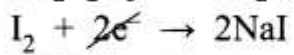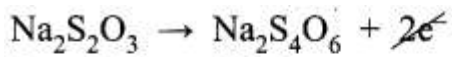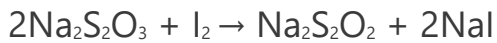
In acidic medium

4. $Zn + NO_3^- \rightarrow Zn^{2+} + NO$

Half reactions are –

$$\overset{o}{Zn} \rightarrow Zn^{2+} \qquad\qquad \text{...............(1)}$$
$$\overset{+5}{NO_3^-} \rightarrow \overset{+2}{NO} \qquad\qquad \text{...............(2)}$$
$$(1) \Rightarrow Zn \rightarrow Zn^{2+} + 2e^- \qquad \text{...............(3)}$$
$$(2) \Rightarrow NO_3^- + 4H^+ \rightarrow NO + 2H_2O \quad \text{...............(4)}$$
$$(3) \times 3 \Rightarrow 3Zn \rightarrow 3Zn^{2+} + \cancel{6e} \qquad\qquad \text{...............(5)}$$
$$(4) \times 2 \Rightarrow 2NO_3^- + \cancel{6e} + 8H^+ \rightarrow 2NO + 4H_2O \qquad \text{...............(6)}$$
$$\overline{3Zn + 2NO_3^- + 8H^+ \rightarrow 3Zn^{2+} + 2NO + 4H_2O}$$
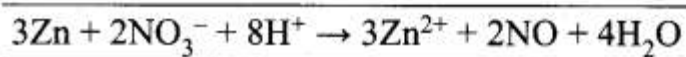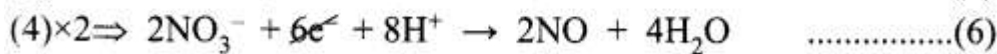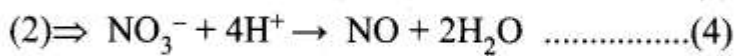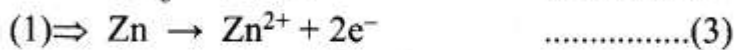
UNIT 2 QUANTUM MECHANICAL MODEL OF ATOM

II. Answer the following.

26. Which quantum number reveal information about the shape, energy, orientation and size of orbitals?

Magnetic quantum number reveal information about the shape, energy, orientation and size of orbitals.

27. How many orbitals are possible for n =4?

If n = 4, the possible number of orbitals are calculated as follows –

n = 4, main shell = N

If n = 4, l values are 0, 1, 2, 3

If l = 0, 4s orbital = 1 orbital

If l = 1, m = -1,0, +1 = 3 orbitals

If l = 2, m = -2,-1,0, +1,+2 = 5 orbitals

If l = 3, m = -3,-2,-1,0, +1,+2,+3 = 7 orbitals

∴ Total number of orbitals = 16 orbitals

28. How many radial nodes for 2s, 4p, 5d and 4f orbitals exhibit? How many angular nodes?

Formula for total number of nodes = n – 1

1. For 2s orbital: Number of radial nodes =1.

2. For 4p orbital: Number of radial nodes = n – l – 1. = 4 – 1 – 1 = 2

Number of angular nodes = l

∴ Number of angular nodes = 1

So, 4p orbital has 2 radial nodes and 1 angular node.

3. For 5d orbital:

Total number of nodes = n – 1 = 5 – 1 = 4 nodes

Number of radial nodes = n – l – 1 = 5 – 2 – 1 = 2 radial nodes.

Number of angular nodes = l = 2

∴ 5d orbital have 2 radial nodes and 2 angular nodes.

4. For 4f orbital:

Total number of nodes = n – 1 = 4 – 1 = 3 nodes

Number of radial nodes = n – 7 – 1 = 4 – 3 – 1 = 0 node.

Number of angular nodes = l = 3 nodes

∴ 4f orbital have 0 radial node and 3 angular nodes.

29. The stabilization of a half filled d-orbital is more pronounced than that of the p-orbital why?

The exactly half filled orbitals have greater stability. The reason for their stability are –

1. symmetry
2. exchange energy.

(1) Symmetry:

The half filled orbitals are more symmetrical than partially filled orbitals and this symmetry leads to greater stability.

(2) Exchange energy:

The electrons with same spin in the different orbitals of the same sub shell can exchange their position. Each such exchange release energy and this is known as exchange energy. Greater the number of exchanges, greater the exchange energy and hence greater the stability. In d-orbital, 10 exchanges are possible but in p-orbital 6 exchanges are possible. So, d – orbital with 5 unpaired electrons (10 exchanges)n i.e. half filled is more stable than p – orbital with 3 unpaired electrons (6 exchanges).

30. Consider the following electronic arrangements for the d^5 configuration.

(a) | ⇅ | ⇅ | ↑ | | |

(b) | ↑ | ↑ | ↑ | ⇅ | |

(c) | ↑ | ↑ | ↑ | ↑ | ↑ |

(1) Which of these represents the ground state

(2) Which configuration has the maximum exchange energy.

(1) (c) | ↑ | ↑ | ↑ | ↑ | ↑ | – This represents the ground state.

(2) (a) | ⇅ | ⇅ | ↑ | | | – This represents the maximum exchange energy.

31. State and explain Pauli's exclusion principle.

Pauli's exclusion principle states that "No two electrons in an atom can have the same set of values of all four quantum numbers".

Illustration: H(Z = 1) $1s^1$.

One electron is present in hydrogen atom, the four quantum numbers are n = 1, l = 0, m = 0 and s =+½. For helium Z = 2. He: $1s^2$. In this one electron has the quantum number same as that of hydrogen, n = 1, l = 0, m = 0 and s = +½ For other electron, fourth quantum number is different, i.e. n = 1, l = 0, m = 0 and s = – ½.

32. Define orbital? What are the n and l values for $3p_x$ and $4 d_{x^2-y^2}$ electron?

(i) Orbital is a three dimensional space which the probability of finding the electron is maximum.

(ii) For $3p_x$ electron   n value = 3

     l value = 1

(iii) For $4d_{x^2-y^2}$ electron   n value = 4

     l value = 2

33. Explain briefly the time independent Schrodinger wave equation?

The time independent Schrodinger equation can be expressed as

$\hat{H} \Psi = E\Psi$ ....(1)

Where $\hat{H}$ is called Hamiltonian operator.

Ψ is the wave function.

E is the energy of the system.

$$\hat{H} = \left[\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right] \quad \ldots\ldots\ldots (2)$$

Since Ψ is a function of position coordinates of the particle and is denoted by Ψ (x, y, z)

∴ Equation (1) can be written as,

$$\left[\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi \right] = E\psi \quad \ldots\ldots\ldots (3)$$

Multiply the equation (3) by Ĥ and rearranging

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad \ldots\ldots\ldots (4)$$

The above equation (4) Schrodinger wave equation does not contain time as a variable and is referred to as time independent Schrodinger wave equation.

34. Calculate the uncertainty in position of an electron, if Δv = 0.1% and n = 2.2 x 10⁶ ms⁻¹.

Mass of an electron = m = 9.1×10^{-31} kg.

Δv = Uncertainty in velocity = $0.1100 \times 2.2 \times 10^3$ ms⁻¹ .

Δv = 0.22×10^4 = 2.2×10^3 ms⁻¹

Δx . Δv . m = $\frac{h}{4\pi}$

Δx = $\frac{h}{\Delta v.m \times 4\pi}$

$$= \frac{6.626 \times 10^{-34}}{2.2 \times 10^3 \times 9.1 \times 10^{-31} \times 4 \times 3.14}$$

$$= \frac{6.626 \times 10^{-34} \times 10^{-3} \times 10^{31}}{2.2 \times 9.1 \times 4 \times 3.14}$$

$$= \frac{6.626 \times 10^{-6}}{251.45}$$

= 0.02635×10^{-6}

Δx = 2.635×10^{-8}

Uncertainty in position = 2.635×10^{-8}.

35. Determine the values of all the four quantum numbers of the 8th electron in O – atom and 15ᵗʰ electron in Cl atom and the last electron in chromium.

(1) O (Z = 8) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Four quantum numbers for $2p_x^1$ electron in oxygen atom:

n = principal quantum number = 2

l = azimuthal quantum number = 1

m = magnetic quantum number = +1

s = spin quantum number = $+\frac{1}{2}$

(2) Cl (Z = 17) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$

Four quantum numbers for 15ᵗʰ electron in chlorine atom:

n = 3, l = 1, m = 0, s = + ½

(3) Cr (Z = 24) $1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^2\ 3d^2\ 4s^1$

n = 3, l = 2, m = +2, s = + ½

36. The quantum mechanical treatment of the hydrogen atom gives the energy value:

$E_n = -13.6n^2$ **eV atom^{-1}**

1. use this expression to find ΔE between n = 3 and n = 4
2. Calculate the wavelength corresponding to the above transition.

(1) When n = 3

$E_3 = -13.63_2 = -13.69 = -1.511$ eV atom^{-1}

When n = 4 $E_4 = -13.64_2 = -0.85$ eV atom^{-1}

ΔE = $E_4 - E_3$ = − 0.85 − (-1.511) = + 0.661 eV atom

ΔE = $E_3 - E_4$

= − 1.511 − (-0.85)

= − 0.661 eV atom^{-1}

(2) Wave length = λ

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E}$$

h = Planck's constant = 6.626 x 10^{-34} Js^{-1}

c = 3 x 10^8 m/s

$$\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.661}$$

$$= 10.02 \times 10^{-34} \times 3 \times 10^8$$

$$= 30 \times 10^{-26}$$

$$\lambda = 3 \times 10^{-25} m$$

37. How fast must a 54 g tennis ball travel in order to have a de Broglie wavelength that is equal to that of a photon of green light 5400 Å?

m = mass of tennis ball = 54 g = 5.4 x 10^{-2} kg.

λ = de Broglie wavelength = 5400 Å. = 5400 x 10^{-10} m.

V = velocity of the ball = ?

$$\lambda = \frac{h}{mV}$$

$$V = \frac{h}{\lambda.m}$$

$$= \frac{6.626 \times 10^{-34}}{5400 \times 10^{-10} \times 5.4 \times 10^{-2}}$$

$$= \frac{6.626 \times 10^{-34} \times 10^{10} \times 10^{2}}{5400 \times 5.4}$$

$$= \frac{6.626 \times 10^{-24}}{54 \times 5.4}$$

$$= \frac{6.626 \times 10^{-24}}{29.6}$$

$= 0.2238 \times 10^{-24}$

$= 2.238 \times 10^{-25}$ m.

38. For each of the following, give the sub level designation, the allowable m values and the number of orbitals.

1. **n = 4, l = 2,**
2. **n = 5, l = 3**
3. **n = 7, l = 0**

1. n = 4, l = 2

If l = 2, 'm' values are -2, -1, 0, +1, +2

So, 5 orbitals such as $d_{xy}, d_{yz}, d_{xz}, d_{x2-y2}$ and d_z

2. n = 5 , l = 3

If l = 3, 'm' values are -3, -2, -1, 0, +1, +2, +3

So, 7 orbitals such as f z, fxz, fyz, fxyz, fz(x2 y2)' ^x(x2-3y2)' ^y(3×2 ??y

3. n = 7 , l = 0

If l = 0, 'm' values are 0. Only one value.

So, 1 orbital such as 7s orbital.

39. Give the electronic configuration of Mn^{2+} and Cr^{3+}

1. Mn (Z = 25)

$Mn \rightarrow Mn^{2+} + 2e^{-}$

Mn^{2+} electronic configuration is 1s $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^5$

2. Cr (Z = 24)

$Cr \rightarrow Cr^{3+} + 3e^{-}$

Cr^{3+} electronic configuration is Is^2 $2s^2$ $2p^6$ $3s^2 3p^6$ $3d^3$

40. Describe the Aufbau principle.

In the ground state of the atoms, the orbitals are filled in the order of their increasing energies. That is the electrons first occupy the lowest energy orbital available to them. Once the lower energy orbitals are completely filled, then the electrons enter the next higher energy orbitals.

The order of filling of various orbitals as per Aufbau principle is –

1 s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d ....

For e.g., K (Z =19)

The electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.
After filling 4s orbital only we have to fill up 3d orbital.

41. A n atom of an element contains 35 electrons and 45 neutrons. Deduce
1. **the number of protons**
2. **the electronic configuration for the element**
3. **All the four quantum numbers for the last electron**

An element X contains 35 electrons, 45 neutrons
1. The number of protons must be equal to the number of electrons. So the number of protons = 35.
2. Number of electrons = 35. So the electronic configuration is
   $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$.
3. The last electron i.e. 5th electron in 4p orbital has the following quantum numbers.
   $n = 4, l = 1, m = +1, s = +\dfrac{1}{2}$

42. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wave length associated with the electron revolving around the nucleus.

In order for the electron wave to exist in phase, the circumference of the orbit should be an integral multiple of the wavelength of the electron wave. Otherwise, the electron wave is out of phase.

$$mvr = nh / 2\pi, 2\pi r = n\lambda,$$

where mvr = angular momentum
where 2πr = circumference of the orbit

n = 3, n = 4

n=3   n=4
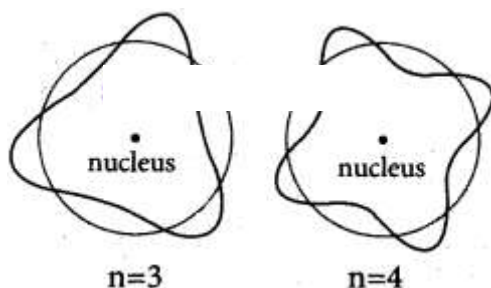
43. Calculate the energy required for the process.
$He^+_{(g)} \rightarrow He^{2+}_{(g)} + e^-$
The ionization energy for the H atom in its ground state is – 13.6 eV atom^{-1}.

The ionization energy for the H atom in its ground state = -13.6 eV atom^{-1}.

Ionization energy $= \dfrac{13.6z^2}{n^2}\ eV$

Z = atomic number
n = principal quantum number or shell number
For He, n = 1, z = 2

$$IE = \dfrac{-16.6 \times 2^2}{1^2} eV$$

44. An ion with mass number 37 possesses unit negative charge. If the ion contains 11.1% more neutrons than electrons. Find the symbol of the ion.

Let the number of electrons in an ion = x

number of neutrons = $n = x + \frac{11.1}{100} eV = 1.111\,x$

(As the number of neutrons are 11.1% more than the number of electrons)

In the neutral of atom, number of electron.

$e^- = x - 1$ (as the ion carries -1 charge)

Similarly number of protons = $P = x - 1$ Number of protons + number of neutrons = mass number = 37

$(x - 1) + 1.111\,x = 37$.

$2.111\,x = 37 + 1$

$2.111\,x = 38$

$$x = \frac{38}{2.111} = 18.009 = 18$$

$\therefore$ *Number of protons* = *atomic number* – 1 = 18 – 1 = 17

$\therefore$ *The symbol of the ion* = $^{37}_{17}Cl.$

45. The Li²⁺ ion is a hydrogen like ion that can be described by the Bohr model. Calculate the Bohr radius of the third orbit and calculate the energy of an electron in 4ᵗʰ orbit.

Li^{2+} hydrogen like ion.

Bohr radius of the third orbit = r_3 = ?

$r_3 = \frac{(0.529)n^2}{Z}$ A

Where n = shell number, Z = atomic number.

$r_3 = \frac{(0.529)3^2}{3}$ A [$\therefore$ for lithium Z = 3, n = 3]

$= \frac{0.529 \times 9}{3}$

$r_3 = 1.587Å$

$E_n = \frac{(-13.6)Z^2}{n^2}$ eV atom⁻¹.

E_4 = Energy of the fourth orbit = ?

$E_4 = \frac{(-13.6) \times 3^2}{4^2} = \frac{-13.6 \times 9}{16} = $ -7.65 eV atom⁻¹

$E_4 = -7.65$ eV atom⁻¹

46. Protons can be accelerated in particle accelerators. Calculate the wavelength (in Å)of such accelerated proton moving at 2.85 × 108 ms⁻¹ (the mass of proton is 1.673 x 10⁻²⁷ Kg).

m = mass of the proton = 1.673 x 10⁻²⁷ Kg

v = velocity of the proton = 2.85 x 10⁸ ms⁻¹

$$\lambda = \frac{h}{mv}$$

h = Planck's constant = 6.626 x 10³⁴ Kg m² s⁻¹

$$= \frac{6.626 \times 10^{-34} \text{ Kg m}^2\text{s}^{-1}}{1.673 \times 10^{-27} \text{ Kg} \times 2.85 \times 10^8 \text{ ms}^{-1}}$$

$$= \frac{6.626 \times 10^{-34} \times 10^{27} \times 10^{-8}}{1.673 \times 2.85} \text{ m}$$

$$= \frac{6.626 \times 10^{-15}}{4.768}$$

$$= 1.389 \times 10^{-15} \text{ m}$$

Wavelength of proton = λ = 1.389 x 10⁻¹⁵ m.

47. What is the de Broglie wavelength (in cm) of a 160g cricket ball travelling at 140 Km hr⁻¹.

m = mass of the cricket ball = 160g = 0.16 kg.

v = velocity of the cricket ball =140 Km h⁻¹

= $140 x^5 18$ = 38.88 ms⁻¹

de Broglie equation = $\lambda = \frac{h}{mv}$

h = Planck's constant = 6.626 x 10⁻³⁴ kg m² s⁻¹

$$= \frac{6.626 \times 10^{-34} \text{ Kg m}^2\text{s}^{-1}}{0.16 \text{ Kg} \times 38.88 \text{ ms}^{-1}}$$

$$\lambda = \frac{6.626 \times 10^{-34}}{6.2208}$$

λ = 1.065 x 10⁻³⁴m

Wave length in cm = 1.065 x 10⁻³⁴ x 100

= 1.065 x 10⁻³² cm.

48. Suppose that the uncertainty in determining the position of an electron in an orbit is 0.6 A. What is the uncertainty in its momentum?

Δx = uncertainty in position of an electron = 0.6 Å = 0.6 x 10⁻¹⁰ m.

Δp = uncertainty in momentum = ?

Heisenberg's uncertainty principle states that,

$$\Delta x . \Delta p \geq \frac{h}{4\pi}$$

$$\Delta p = \frac{h}{4\pi . \Delta x}$$

h = Planck's constant = 6.626 x 10⁻³⁴ kg m² s⁻¹

$$\therefore \Delta p = \frac{6.626 \times 10^{-34} \text{ Kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 0.6 \times 10^{-10} \text{ m}}$$

$$= \frac{6.626 \times 10^{-34} \times 10^{10}}{7.536}$$

Uncertainty in momentum = 0.8792 x 10⁻²⁴ kg ms⁻¹ (or) = 8.792 x 10⁻²⁵ kg ms⁻¹

49. Show that if the measurement of the uncertainty in .the location of the particle is equal to its de Broglie wavelength, the minimum uncertainty in its velocity is equal to its velocity /4π

Answer:

If, uncertainty in position = $\Delta x = \lambda$, the value of uncertainty in velocity = $\frac{v}{4\pi}$

Heisenberg's principle states that

$$\Delta x . \Delta v . m = \frac{h}{4\pi} \ \ldots\ldots\ldots\ldots(1)$$

de Broglie equation states that

$$\lambda = \frac{h}{mv} \ \ldots\ldots\ldots\ldots(2)$$

$\therefore$ h = λ .m.v ....(3)

$\Delta x = h\Delta v. 4\pi$ ....(4)

Substituting the value of h in equation (4)

$$\Delta x = \frac{\lambda x m.v}{\Delta v.4\pi.m}$$

if $\Delta x = \lambda$

$$\Delta v = \frac{\lambda . m.v}{\lambda .4\pi . m} = \frac{v}{4\pi}$$

50. What is the de Broglie wave length of an electron, which is accelerated from the rest, through a potential difference of 100V?

Potential difference = V = 100 V

Potential energy = eV = 1.609 x 10⁻¹⁹c x 100V

$$\frac{v}{4\pi} m v^2 = 1.609 \times 10^{-19} \times 100V$$

$$\frac{v}{4\pi} mv^2 = 1.609 \times 10^{-19} J$$

$$v^2 = 2 \times 1.609 \times 10^{-17} m$$

m = mass of electron = 9.1 x 10⁻³¹ Kg

$$\therefore v^2 = \frac{2 \times 1.609 \times 10^{-17}}{9.1 \times 10^{-31}}$$

$$\therefore v = \sqrt{\frac{2 \times 1.609 \times 10^{-17}}{9.1 \times 10^{-31}}}$$

$$= \sqrt{\frac{2 \times 1.609 \times 10^{-17} \times 10^{31}}{9.1}}$$

$$v = \sqrt{\frac{3.218 \times 10^{14}}{9.1}}$$

v = 5.93 x 10⁶ m/s

$$\lambda = \frac{h}{mv} \ where \ h = 6.626 \times 10^{-34} JS$$

$$= 6.626 \times 10^{-34} \times 9.1 \times 10^{-31} \times 5.93 \times 10^{6}$$

$$= 1.2 \times 10^{-10} m$$

$A = 1.2$ Å.

51. Identify the missing quantum numbers and the sub energy level

n	l	m	Sub energy level
?	?	0	4d
3	1	0	?
?	?	?	5p
?	?	−2	3d

Answer:

n	l	m	Sub energy level
4	2	0	4d
3	1	0	3p
5	1	−1	5p
3	2	−2	3d

20

24. Define modern periodic law.

The modem periodic law states that, "The physical and chemical properties of the elements are periodic function of their atomic numbers."

25. What are isoelectronic ions? Give examples.

There are some ions of different elements having the same number of electrons are called isoelectronic ions.

Example:

Na^+, Mg^{2+}, Al^{3+}, F^-, O^{2-} and N^{3-}

26. What is effective nuclear charge?

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge.

$Z_{eff} = Z - S$

Where,

Z = Atomic number

S = Screening constant calculated by using Slater's rules.

27. Is the definition given below for ionization enthalpy is correct?

"Ionization enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom"

No. It is not correct. The accurate and absolute definition is as follows:

Ionization energy is defined as the minimum amount of energy required to remove the most loosely bound electron from the valence shell of the isolated neutral gaseous atom in its ground state.

28. Magnesium loses electrons successively to form Mg^+, Mg^{2+} and Mg^{3+} ions. Which step will have the highest ionization energy and why?

$$Mg_{(g)} \rightarrow Mg^+ + e\,(I.E_1 = X_1)$$
Neutral atom
$$(Dbt: e\ or\ e^-)$$
$$Mg^+ \rightarrow Mg^{2+} + e^-\,(I.E_2 = X_2)$$
Unipositive cation
$$Mg^{2+} \rightarrow Mg^{3+} + e^-\,(I.E_3 = X_3)$$
Dipositive cation
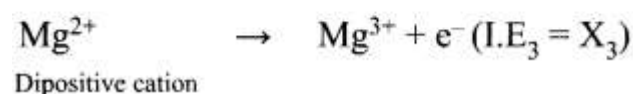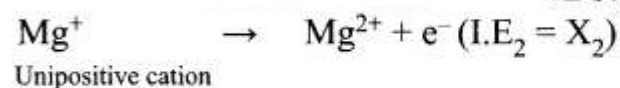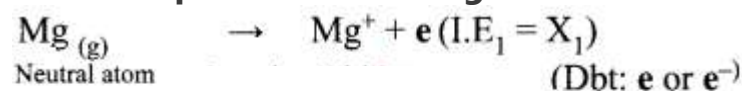
- The third step will have the highest ionization energy. $I.E_3 > I.E_2 > I.E_1$
- Because from a neutral gaseous atom, the electron removal is easy and less amount of energy is required. But from a di positive cation, there will be more number of protons than the electrons and there is more forces of attraction between the nucleus and electron. So the removal of electron in a di positive cation, becomes highly difficult and more energy is required.

29. Define electro negativity.

Electro negativity is the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

30. How would you explain the fact that the second ionization potential is always higher than first ionization potential?

Second ionization potential is always higher than first ionization potential.

- Removal of one electron from the valence orbit of a neutral gaseous atom is easy so first ionization energy is less. But from a uni positive ion, removal of one more electron becomes difficult due to the more forces of attraction between the excess of protons and less number of electrons.
- Due to greater nuclear attraction, second ionization energy is higher than first ionization energy.

31. Energy of an electron in the ground state of the hydrogen atom is -2.18 x 10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of kJ mol^{-1}.

Energy of an electron in the ground state of the hydrogen atom = -2.18 x 10^{-18} J

$H \rightarrow H^+ + e^-$
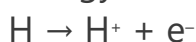
Energy required to ionize 1 mole of hydrogen atoms, we multiply by the Avogadro constant.

E = 2.18 x 10^{-18} x 6.022 × 10^{23}

$= 13.123 \times 10^5 Jmol^{-1}$

$I.E = +1312 KJ\ mol^{-1}$

32. The electronic configuration of an atom is one of the important factor which affects the value of ionization potential and electron gain enthalpy. Explain.

Electronic configuration of an atom affects the value of ionization potential and electron gain enthalpy.

- Half filled valence shell electronic configuration and completely filled valence shell electronic configuration are more stable than partially filled electronic configuration.
- For e.g. Beryllium (Z = 4) 1s^2 2s^2 (completely filled electronic configuration) Nitrogen (Z = 7) 1s^2 2s^2 2p$_x^1$ 2p$_y^1$ 2p$_z^1$ (half filled electronic configuration) Both beryllium and nitrogen have high ionization energy due to more stable nature.
- In the case of beryllium (1s^2 2s^2), nitrogen (1s^2 2s^2 2p^3) the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.
- Noble gases have stable ns^2 np^6 configuration and the addition of further electron is unfavorable and they have zero electron affinity.

33. In what period and group will an element with Z = 118 will be present?

The element with atomic number Z = 118 is present in 7th period and 18th group.

34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.

Fifth period of the periodic table have 18 elements. 5th period starts from Rb to Xe (18 elements). 5th period starts with principal quantum number n = 5 and 1 = 0, 1,2,3 and 4. When n = 5, the number of orbitals = 9.

1 for 5s

5 for 4d

3 for 5p

Total number of orbitals = 9.

Total number of electrons that can be accommodated in 9

orbitals = 9 x 2 = 18. Hence the number of elements in 5th period is 18.

35. Elements a, b, c and d have the following electronic configurations:

a : 1s², 2s², 2p⁶

b : 1s², 2s², 2p⁶, 3s², 3p¹

c : 1s², 2s², 2p⁶ 3s²,3p⁶

d : 1s², 2s², 2p¹

Which elements among these will belong to the same group of periodic table?

Answer:

		Element
a: $1s^2, 2s^2, 2p^6$	(Z = 10)	Ne
b: $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$	(Z = 13)	Al
c: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$	(Z = 18)	Ar
d: $1s^2, 2s^2, 2p^1$	(Z = 5)	B

1. In the above elements, Ne and Ar belong to same group (Noble gases – 18th group).
2. Al and B belong to the same group (13th group).

36. Give the general electronic configuration of lanthanides and actinides?

The electronic configuration of lanthanides is $4f^{1-14}5d^{0-1}6s^2$.

- The electronic configuration of actinides is $5f^{1-14}6d^{0-1}7s^2$

37. Why halogens act as oxidizing agents?

Halogens act as oxidizing agents. Their electronic configuration is $ns^2\,np^5$. So all the halogens are ready to gain one electron to attain the nearest inert gas configuration. An oxidizing agent is the one which is ready to gain an electron. So all the halogens act as oxidizing agents. Also halogens are highly electro negative with low dissociation energy and high negative electron gain enthalpies. Therefore, the halogens have a high tendency to gain an electron. Hence they act as oxidizing agents.

38. Mention any two anomalous properties of second period elements.

In the 1st group, lithium forms compounds with more covalent character while the other elements of this group form only ionic compounds.

- In the 2nd group, beryllium forms compounds with more covalent character while the other elements of this family form only ionic compounds.

39. Explain the Pauling's method for the determination of ionic radius.

1. Ionic radius is defined as the distance from the center of the nucleus of the ion up-to which it exerts its influence on the electron cloud of the ion.

2. Ionic radius of uni-univalent crystal can be calculated from the inter-ionic distance

between the nuclei of the cation and anion.

3. Pauling assumed that ions present in a crystal lattice are perfect spheres and they are in contact with each other, therefore

$$d = r_{C+} + r_{A-} \quad .....(1)$$

Where, d = distance between the center of the nucleus of cation C+ and the anion A-

r_{C+} = radius of cation

r_{A-} = radius of anion.

4. Pauling assumed that the radius of the ion having noble gas configuration (Na$^+$ and F$^-$ having 1s^2, 2s^2, 2p^6 configuration) is inversely proportional to the effective nuclear charge felt at the periphery of the ion.

$$i.e. \; r_{C+} \propto \frac{1}{(Z_{eff})_{C+}} \quad ....(2)$$

$$r_{A-} \propto \frac{1}{(Z_{eff})_{A-}} \quad ....(3)$$

Where Z_{eff} is the effective nuclear charge

$$Z_{eff} = Z - S$$

5. Dividing the equation (2) by (3)

$$\frac{r_{C+}}{r_{A-}} = \frac{(Z_{eff})_{A-}}{(Z_{eff})_{C+}} \quad ....(4)$$

On solving equation (1) and (4), the values of r_{C+} and r_{A-} can be obtained.

40. Explain the periodic trend of ionization potential.

(a) The energy required to remove the most loosely held electron from an isolated gaseous atom is called as ionization energy.

(b) Variation in a period:

Ionization energy is a periodic property. On moving across a period from left to right, the ionization enthalpy value increases. This is due to the following reasons.

- Increase of nuclear charge in a period
- Decrease of atomic size in a period

Because of these reasons, the valence electrons are held more tightly by the nucleus. Therefore, ionization enthalpy increases.

(c) Variation in a group:

As we move from top to bottom along a group, the ionization enthalpy decreases. This is due to the following reasons.

- A gradual increase in atomic size
- Increase of screening effect on the outermost electrons due to the increase of number of inner electrons.

Hence, ionization enthalpy is a periodic property.

41. Explain the diagonal relationship.

On moving diagonally across the periodic table, the second and the third period elements show certain similarities.

- Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.

  Li   Be   B   C

- Na   Mg   Al Si
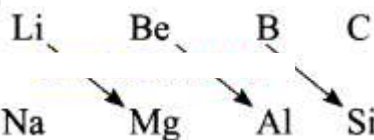
- The similarity in properties existing between the diagonally placed elements is called "diagonal relationship".

42. Why the first ionization enthalpy of sodium is lower than that of magnesium while its second ionization enthalpy is higher than that of magnesium?

The 1st ionization enthalpy of magnesium is higher than that of Na due to higher nuclear charge and slightly smaller atomic radius of Mg than Na. After the loss of first electron, Na^+ formed has the electronic configuration of neon (2,8). The higher stability of the completely filled noble gas configuration leads to very high second ionization enthalpy for sodium. On the other hand, Mg^+ formed after losing first electron still has one more electron in its outermost (3 s) orbital. As a result, the second ionization enthalpy of magnesium is much smaller than that of sodium.

43. By using Pauling's method calculate the ionic radii of K^+ and Cl^- ions in the potassium chloride crystal. Given that $d_{K^+-Cl^-}$ = 3.14 Å

Given

$$d_{K^+-Cl^-} = 3.14 \text{ Å}$$
$$r_{K^+} = ? \qquad r_{Cl^-} = ?$$

i.e. $r_{K^+} + r_{Cl^-} = 3.14 Å$ ....(1)

We know that,

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{(Z_{eff})_{Cl^-}}{(Z_{eff})_{K^+}}$$

$(Z_{eff})_{Cl^-} = Z - S$

$= 17 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]$

$= 17 - 11.25 = 5.75$

$(Z_{eff})_{K^+} = Z - S$

$= 19 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)]$

$= 19 - 11.25 = 7.75$

$$\therefore \frac{r_{(K^+)}}{r_{(Cl^-)}} = \frac{(Z_{eff})_{Cl^-}}{(Z_{eff})_{K^+}} = \frac{5.75}{7.75} = 0.74$$

$r_{(K^+)} = 0.74 \, r_{(Cl^-)}$

Substitute the value of $r_{(K^+)}$ in equation (1)

$0.74 \, r_{(Cl^-)} + r_{(Cl^-)} = 3.14 \text{ Å}$

$1.74 \, r_{(Cl^-)} = \frac{3.14 Å}{1.74} = 1.81 \text{ Å}.$

44. Explain the following, give appropriate reasons.

1. **Ionization potential of N is greater than that of O**
2. **First ionization potential of C-atom is greater than that of B-atom, where as the reverse is true for second ionization potential.**
3. **The electron affinity values of Be, Mg and noble gases are zero and those of N (0.02 eV) and P (0.80 eV) are very low**
4. **The formation of F⁻ (g) from F(g) is exothermic while that of O²⁻(g) from O (g) is endothermic.**

1. N (Z = 7) $1s^2 2s^2 2p_x^1 12p_y^1 2p_z^1$. It has exactly half filled electronic configuration and it is more stable. Due to stability, ionization energy of nitrogen is high.

O (Z = 8) $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. It has incomplete electronic configuration and it requires less ionization energy.

$I.E_1$ N > $I.E_1$O

2. C (Z = 6) $1s^2 2s^2 2p_x^1 2p_y^1$. The electron removal from p orbital is very difficult. So carbon has highest first ionization potential. B (Z = 5) $1s^2 2s^2 2p^1$. In boron nuclear charge is less than that of carbon, so boron has lowest first ionization potential.

$I.E_1$ C > $I.E_1$ B

But it is reverse in the case of second ionization energy. Because in case of B+ the electronic configuration is $1s^2 2s^2$, which is completely filled and it has high ionization energy. But in C+ the electronic configuration is $1s^2 2s^2 2p^1$, one electron removal is easy so it has low ionization energy.

$I.E_2$ B > $I.E_2$ C

3. Be (Z = 4) $1s^2 2s^2$

Mg (Z = 12) $1s^2 2s^2 2p^6 3s^2$

Noble gases has the electronic configuration of $ns^2 np^6$. All these are completely filled and are more stable. For all these elements Be, Mg and noble gases, addition of electron is unfavorable and so they have zero electron affinity.

Nitrogen (Z = 7) $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. It has half filled electronic configuration. So addition of electron is unfavorable and it has very low electron affinity value of 0.02 eV. Phosphorus (Z = 15) $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$. It also has half filled electronic configuration. Due to the symmetry and more stability, it has very low electron affinity value of 0.80 eV.

4. $F_{(g)} + e^- \rightarrow F_{(g)}^-$ exothermic

F (Z = 9) $1s^2 2s^2 2p^5$. It is ready to gain one electron to attain the nearest inert gas configuration. By gaining one electron, energy is released, so it is an exothermic reaction.

$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)}$ endothermic

O (Z = 8) $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. It is the small atom with high electron density. The first electron affinity is negative because energy is released in the process of adding one electron to the neutral oxygen atom. Second electron affinity is always endothermic

(positive) because the electron is added to an ion which is already negative, therefore it must overcome the repulsion.

45. What is screening effect? Briefly give the basis for Pauling's scale of electro negativity. Screening effect:

The repulsive force between inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect (or) screening effect.

Pauling's scale:

- Electro negativity is the relative tendency of an element present in a covalently bonded molecule to attract the shared pair of electrons towards itself.
- Pauling assigned arbitrary value of electronegativities for hydrogen and fluorine as 2.2 and 4, respectively.
- Based on this the electronegativity values for other elements can be calculated using the following expression.

  $(X_A - X_B) = 0.182 \sqrt{E_{AB} - (E_{AA} \, E_{BB})}$

  Where E_{AB}, E_{AA} and E_{BB} are the bond dissociation energies of AB, A_2 and B_2 molecules respectively.

  X_A and X_B are electronegativity values of A and B.

46. State the trends in the variation of electro negativity in period and group. Variation of electron negativity in a period:

The electro negativity increases across a period from left to right. Since the atomic radius decreases in a period, the attraction between the valence electron and the nucleus increases. Hence the tendency to attract shared pair of electrons increases. Therefore, electro negativity increases in a period.

Variation of Electronegativity along I period
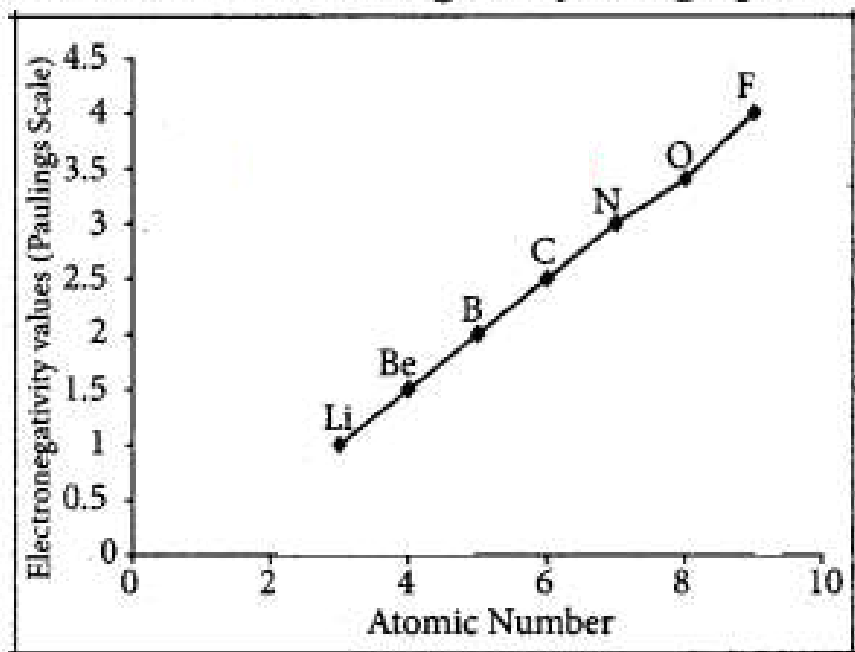
Variation of electro negativity in a group:

The electro negativity decreases down a group. As we move down a group, the atomic radius increases and the nuclear attractive force on the valence electron decreases. Hence electro negativity decreases in a group.

28
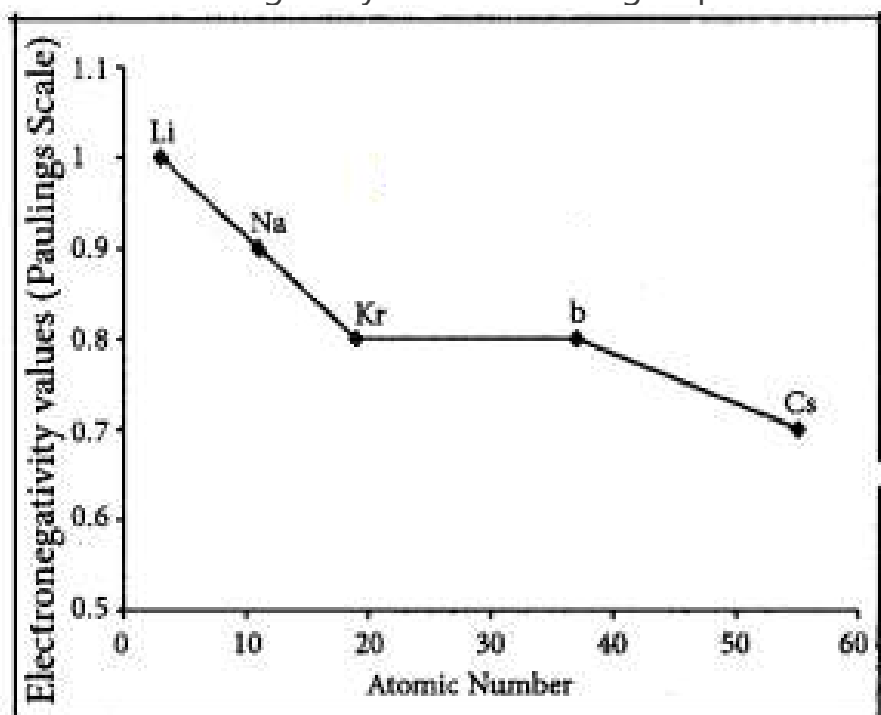
UNIT 4 HYDROGEN

II. Write brief answer to the following questions

22. Explain why hydrogen is not placed with the halogen in the periodic table.
- Hydrogen resembles alkali metals as well as halogens.
- Hydrogen resembles more alkali metals than halogens.
- Electron affinity of hydrogen is much less than that of halogen atom. Hence the tendency to form hydride ion is low compared to that of halogens.
- In most of its compounds hydrogen exists in +1 oxidation state. Therefore it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

23. The cube at 0°C is placed in some liquid water at 0°C, the ice cube sinks – Why?
- In an ice cube, each atom is surrounded tetrahedrally by four water molecules through hydrogen bond and its density is low.
- Liquid water at 0°C has the density as 999.82 kg/cm^3. Maximum density is attained by water only at 4°C as 1000 kg/cm^3.
- When the temperature changed from 4°C to 0°C, the density of water decreases rather than increases. This is called anomalous expansion of water.
- The reason for this phenomenon lies in the structure of ice lattice and hydrogen bonding in water.
- At 0°C, ice cube sinks in liquid water at 0°C because of the lesser density and greater volume of water.

24. Discuss the three types of Covalent hydrides.
1. They are the compounds in which hydrogen is attached to another element by sharing of electrons.
2. The most common examples of covalent hydrides are methane, ammonia, water and hydrogen chloride.
3. Molecular hydrides of hydrogen are further classified into three categories as,
   - Electron precise (CH_4, C_2H_6 , SiH_4 , GeH_4)
   - Electron-deficient (B_2H_6) and
   - Electron-rich hydrides (NH_3 , H_2O)
4. Since most of the covalent hydrides consist of discrete, small molecules that have relatively weak intermolecular forces, they are generally gases or volatile liquids.

25. Predict which of the following hydrides is a gas on a solid (a) HCl (b) NaH. Give your reason.
At room temperature, HCl is a colourless gas and the solution of HCl in water is called hydrochloric acid and it is in liquid state.

- Sodium hydride NaH is an ionic compound and it is made of sodium cations (Na^+) and hydride (H^-) anions. It has the octahedral crystal structure. It is an alkali metal hydride.

26. Write the expected formulas for the hydrides of 4th period elements. What is the trend in the formulas? In what way the first two numbers of the series different from the others ?

The expected formulas for the hydrides of 4th period elements MH_4 (electron precise). M_2H_6 (electron deficient) and MH_3 (electron rich).

The trend in formula is –

- Electron precise hydrides – CH_4 C_2H_6, SiH_4, GeH_4
- Electron deficient hydrides – B_2H_6
- Electron rich hydrides – NH_3, H_2O

The first two members of the series KH, CaH_2 are ionic hydrides whereas the other members of the series CH_4, C_2H_6, SiH_4, B_2H_6, NH_3 are covalent hydrides.

27. Write chemical equation for the following reactions.
1. **reaction of hydrogen with tungsten (VI) oxide NO_3 on heating.**
2. **hydrogen gas and chlorine gas.**

1. $3H_2 + WO_2 \rightarrow W + 3H_2O$

   Hydrogen reduces tungsten (VI) oxide. WO_3 to tungsten at high temperature.
2. $H_2 + Cl_2 \rightarrow 2HCl$ (Hydrogen Chloride)
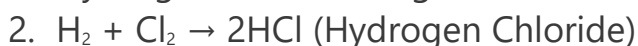
   Hydrogen reacts with chlorine at room temperature under light to give hydrogen chloride.

28. Complete the following chemical reactions and classify them in to (a) hydrolysis (b) redox (c) hydration reactions.
1. **$KMnO_4 + H_2O_2 \rightarrow$**
2. **$CrCl_3 + H_4O \rightarrow$**
3. **$CaO + H_2O \rightarrow$**

1. $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 2KOH + 3H_2O + 3O_{2(g)}$

   This reaction is a redox reaction.
2. $CrCl_3 + 6H_2O_2 \rightarrow [Cr(H_2O)_6)] Cl_3$
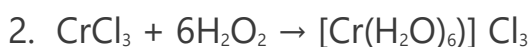
   This reaction is a hydration reaction.
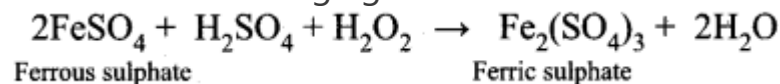3. $CaO + H_2O \rightarrow Ca(OH)_2$
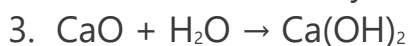
   This reaction is a hydrolysis reaction.

29. Hydrogen peroxide can function as an oxidizing agent as well as reducing agent. Substantiate this statement with suitable examples.

Hydrogen peroxide can function as an oxidizing agent as well as reducing agent.

- H_2O_2 act as oxidizing agent in acidic medium. For example,

$$\underset{\text{Ferrous sulphate}}{2FeSO_4} + H_2SO_4 + H_2O_2 \rightarrow \underset{\text{Ferric sulphate}}{Fe_2(SO_4)_3} + 2H_2O$$

- H_2O_2 act as reducing agent in basic medium. For example,

$$2KMnO_{4\ (aq)} + 3H_2O_{2\ (aq)} \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_{2\ (g)}$$
Potassium permanganate   Manganese dioxide

30. Do you think that heavy water can be used for drinking purposes ?

- Heavy water (D_2O) contains a proton and a neutron. This makes deuterium about twice as heavy as protium, but it is not radioactive. So heavy water is not radioactive.
- If you drink heavy water, you don't need to worry about radiation poisoning. But it is not completely safe to drink, because the biochemical reaction in our cells are affected by the difference in the mass of hydrogen atoms.
- If you drink an appreciable volume of heavy water, you might feel dizzy because of the density difference. It would change the density of fluid in your inner ear. So it is unlikely to drink heavy water.

31. What is water-gas shift reaction?

The carbon monoxide of water gas can be converted to carbon dioxide by mixing the gas mixture with more steam at 400°C and passed over a shift converter containing iron/copper catalysts. This reaction is called water-gas shift reaction.

$CO + H_2O \rightarrow CO_2 + H_2\uparrow$
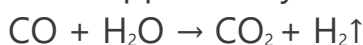
32. Justify the position of hydrogen in the periodic table?

Hydrogen resembles alkali metals in the following aspects.

1. Electronic configuration Is^1 as alkali metals have ns^1.
2. Hydrogen forms unipositive H+ ion like alkali metals Na^+, K^+.
3. Hydrogen form halides (HX), oxides (H_2O) peroxide (H_2O_2) like alkali metals (NaX. Na_2O, Na_2O_2).
4. Hydrogen also acts as reducing agent like alkali metals. Hydrogen resembles halogens in the following aspects.
5. Hydrogen has a tendency to gain one electron to form hydride ion (H^-) as halogens to form halide ion. (X^-).
6. Comparing the properties of hydrogen with alkali metals and with halogens, we can conclude that hydrogen resembles more alkali metals. In most of the compounds hydrogen exist in +1 oxidation state.
7. Therefore, it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

33. What are isotopes? Write the names of isotopes of hydrogen.

1. Isotopes are atoms of the same element that have the same atomic number but having different mass numbers (or) Isotopes are atoms with the same number of protons and electrons but differ in number of neutrons.

2. Hydrogen has three naturally occuring isotopes namely Protium ($_1H^1$), Deuterium ($_1H^2$) and Tritium ($_1H^3$).

Protium

Deuterium   Tritium
Isotopes of hydrogen
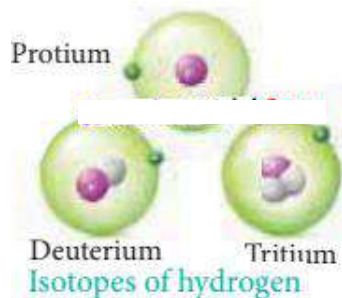
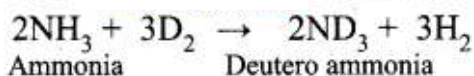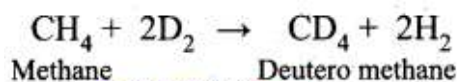## 34. Give the uses of heavy water.
1. Heavy water is used as moderator in nuclear reactors as it can lower the energies of fast moving neutrons.
2. D_2O is commonly used as an tracer to study organic reaction mechanisms and mechanism of metabolic reactions.
3. It is also used as a coolant in nuclear reactors as it absorbs the heat generated.

35. Explain the exchange reactions of deuterium.
Deuterium can replace reversibly hydrogen in compounds either partially or completely depending upon the reaction conditions. These reactions occur in the presence of deuterium.

$$CH_4 + 2D_2 \rightarrow CD_4 + 2H_2$$
Methane   Deutero methane

$$2NH_3 + 3D_2 \rightarrow 2ND_3 + 3H_2$$
Ammonia   Deutero ammonia

36. How do you convert para hydrogen into ortho hydrogen ?
Para hydrogen can be converted into ortho hydrogen by the following ways:
- By treating with catalysts platinum or iron.
- By passing an electric discharge
- By heating > 800°C.
- By mixing with paramagnetic molecules such as O_2, NO, NO_2.
- By treating with nascent/atomic hydrogen.

37. Mention the uses of deuterium.
- Deuterium is used as a tracer element.
- Deuterium is used to study the movement of ground water by isotopic effect.

38. Explain preparation of hydrogen using electrolysis.
High purity of hydrogen (>99.9%) is obtained by the electrolysis of water containing traces of acid or alkali or electrolysis of aqueous solution of sodium hydroxide or potassium hydroxide using a nickel anode and iron cathode. This process is not economical for large scale production.

At anode : $2OH^- \rightarrow H_2O + \frac{1}{2} O_2 + 2e^-$
At cathode : $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
Overall reaction : $H_2O \rightarrow H_2 + 14 O_2$
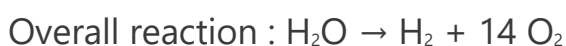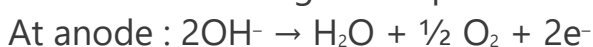
39. A groups metal (A) which is present in common salt reacts with (B) to give compound (C) in which hydrogen is present in -1 oxidation state. (B) on reaction with a gas (C) to give universal solvent (D). The compound (D) on reacts with (A) to give (B), a strong base. Identify A, B, C, D and E. Explain the reactions.
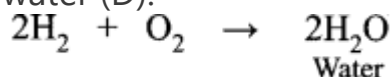
1.Group (1) metal (A) is present in common salt NaCl. So, (A) is sodium – Na.

2. Sodium reacts with hydrogen (B) to give sodium hydride – NaH (C) in which hydrogen is in -1 oxidation state.

$$2Na + H_2 \rightarrow 2NaH$$
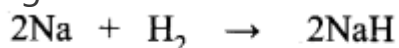
Sodium (A) Hydrogen (B) Sodium hydride (C)

3. Hydrogen on reaction with oxygen (O_2) gas which is (C) to give a universal solvent water (D).

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

Water

4. Water (D) reacts with sodium metal (A) to give a strong base sodium hydroxide NaOH which is (E).

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$
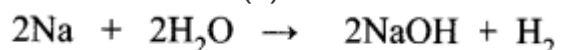
Sodium hydroxide(E)

| A	Sodium	Na
B	Hydrogen	H_2
C	Oxygen	O_2
D	Water	H_2O
E	Sodium hydroxide	NaOH

40. An isotope of hydrogen (A) reacts with diatomic molecule of element which occupies group number 16 and period number 2 to give compound (B) is used as a modulator in nuclear reaction. (A) adds on to a compound (C), which has the molecular formula C_3H_6 to give (D). Identify A, B, C and D.

1. An isotope of hydrogen Deuterium (A) reacts with diatomic molecule of element belongs to group number 16 and period number 2 oxygen O_2 to give a compound (B) which is heavy water D_2O. D_2O is used as a moderator in nuclear reaction.

$$2D_2 + O_2 \rightarrow 2D_2O$$
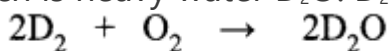
Deuterium (A)   Heavy water (B)

2. Deuterium reacts with C_3H_6 propane (C) to give Deutero propane C_2D_6 (D).

$$3D_2 + C_3H_6 \rightarrow C_3D_6 + 3H_2$$

Propane   Deutero propane
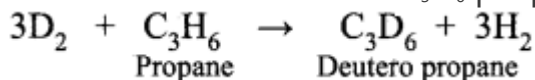
A	Deuterium	D_2
B	Heavy water	D_2O
C	Propane	C_3H_6
D	Deutero propane	C_3D_6

41. NH_3 has exceptionally high melting point and boiling point as compared to those of the hydrides of the remaining element of group 15 Explain.

33

1. NH$_3$ has exceptionally high melting point and boiling point due to hydrogen bonding between NH$_3$ molecules.
2. Each molecule can form a maximum of 4 hydrogen bonds but on average 1 hydrogen bond per molecule as there is only one lone pair on NH$_3$ available for hydrogen bonding.
3. Hydrogen bonding is strong intermolecular attraction as H on NH$_3$ acts like a proton due to partial positive on it whole N has the partial negative charge. Thus when the very polarized H comes close to a N atom in another NH$_3$ molecule, a very strong hydrogen bond is formed.
4. Due to much strong intermolecular interactions compared to weaker permanent dipole-dipole interactions between other XH$_3$ molecules in group 15, large amount of energy are required to overcome the forces, giving it the highest boiling point and highest melting point.

42. Why interstitial hydrides have a lower density than the parent metal.

- d block elements form metallic or interstitial hydrides, on heating with dihydrogen under pressure.
- Hydrogen atom being small in size occupy some in the metallic lattice producing distortion without any change in its type.
- The densities of these hydrides are lower than those of metals from which they are formed since the crystal lattice expands due to the inclusion of dihydrogen.

## 43. How do you expect the metallic hydrides to be useful for hydrogen storage?

- In metallic hydrides, hydrogen is adsorbed as H-atoms. Due to the adsorption of H atoms the metal lattice expands and become unstable.
- Thus, when metallic hydride is heated, it decomposes to form hydrogen and finely divided metal.
- The hydrogen evolved can be used as fuel.

44. Arrange NH$_3$, H$_2$O and HF in the order of increasing magnitude of hydrogen bonding and explain the basis for your arrangement.

- Increasing magnitude of hydrogen bonding among NH$_3$, H$_2$O and HF is HF>H$_2$O>NH$_3$
- The extent of hydrogen bonding depends upon electronegativity and the number of hydrogne atoms available for bonding.
- Among N, F nd O the increasing order of their electronegativities are N<O H$_2$O>NH$_3$.

45. Compare the structures of H$_2$O and H$_2$O$_2$.

In water, O is sp^3 hybridized. Due to stronger lone pair-lone pair repulsions than bond pair-bond pair repulsions, the HOH bond angle decreases from 109.5° to 104.5°. Thus water molecule has a bent structure.
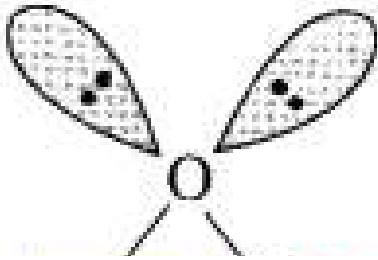
H_2O_2 has a non-planar structure. The $0 - H$ bonds are in different planes. Thus, the structure of H_2O_2 is like an open book.
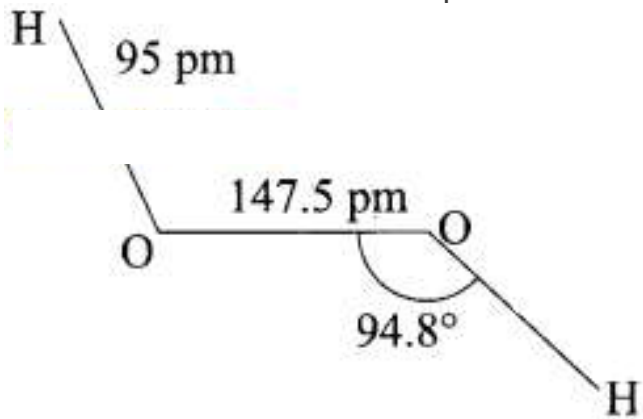
UNIT 5 ALKALI AND ALKALINE EARTH METALS

II. Write brief answer to the following questions

26. Why sodium hydroxide is much more water soluble than chloride?

$NaOH + H_2O \rightleftharpoons Na^+ + OH^-$

1. This reaction is an exothermic reaction. Sodium hydroxide being a strong base, completely dissociated in aqueous medium. The heat evolved increases the stability. This phenomenon is strong enough to prove that sodium hydroxide crystals are readily dissolved in water.

2. NaCl is geologically stable. If kept dry, it will remain a free flowing solid for years. Water can dissolve NaCl because the Na^+ ions are attracted by OH^- in water and Cl^- ions are attracted by H^+ in water. The solubility of NaCl does not increase the temperature. Based on this, NaOH is much more soluble due to exothermic nature than sodium chloride.

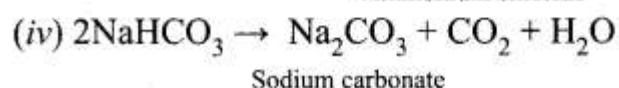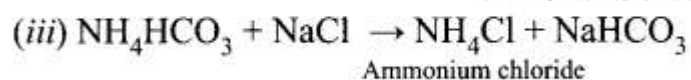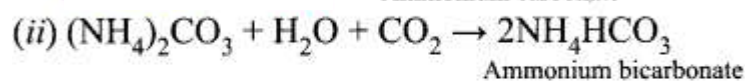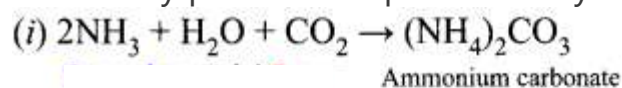**27. Explain what to meant by efflorescence?**

Efflorescence is the formation of powdery deposit on the surface of rock as a result of loss of moisture or water on exposure to air.

1. Efflorescence is the formation of whitish powdery deposit on the surface of rocks like gypsum in dry regions. It is formed as mineral rich water, rises to the surface through capillary action and then evaporates.

2. Gypsum crystals are sometimes found to occur in the form that resembles the petals of flower. This happens mostly in arid areas or desert terrains, where there is rapid loss of water. This phenomenon is called as efflorescence.

28. Write the chemical equations for the reactions involved in Solvay process of preparation of sodium carbonate.

Solvay process:

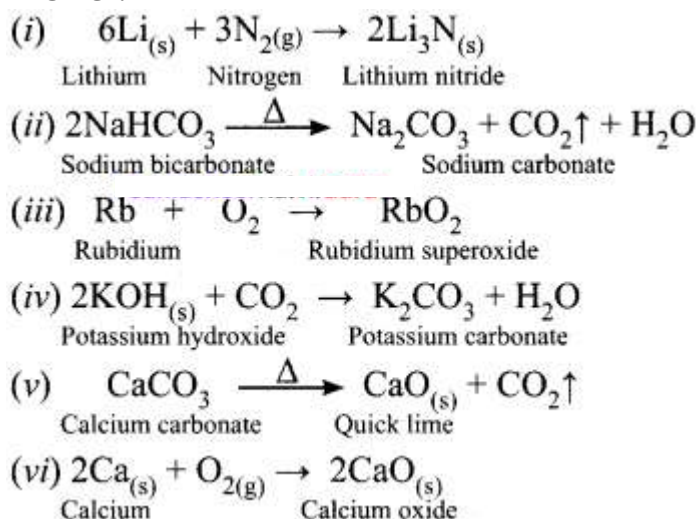The Solvay process is represented by the below chemical equations:

$$(i)\ 2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$
$$\text{Ammonium carbonate}$$

$$(ii)\ (NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$
$$\text{Ammonium bicarbonate}$$

$$(iii)\ NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$
$$\text{Ammonium chloride}$$

$$(iv)\ 2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$
$$\text{Sodium carbonate}$$

29. An alkali metal (x) forms a hydrated sulphate, X_2SO_2. $10H_2O$. Is the metal more likely to he sodium (or) potassium.

X forms X_2SO_2. $10H_2O$. The metal is more likely be sodium. So X is Na_2SO_4. $10H_2O$. It is otherwise called as Glauber's salt.

30. Write balanced chemical equation for each of the following chemical reactions.
(i) Lithium metal with nitrogen gas
(ii) Heating solid sodium bicarbonate
(iii) Rubidium with oxygen gas
(iv) Solid potassium hydroxide with CO_2
(v) Heating calcium carbonate
(vi) Heating calcium with oxygen
Answer:

$(i) \quad \underset{\text{Lithium}}{6Li_{(s)}} + \underset{\text{Nitrogen}}{3N_{2(g)}} \rightarrow \underset{\text{Lithium nitride}}{2Li_3N_{(s)}}$

$(ii) \quad \underset{\text{Sodium bicarbonate}}{2NaHCO_3} \xrightarrow{\Delta} \underset{\text{Sodium carbonate}}{Na_2CO_3} + CO_2\uparrow + H_2O$

$(iii) \quad \underset{\text{Rubidium}}{Rb} + O_2 \rightarrow \underset{\text{Rubidium superoxide}}{RbO_2}$

$(iv) \quad \underset{\text{Potassium hydroxide}}{2KOH_{(s)}} + CO_2 \rightarrow \underset{\text{Potassium carbonate}}{K_2CO_3} + H_2O$

$(v) \quad \underset{\text{Calcium carbonate}}{CaCO_3} \xrightarrow{\Delta} \underset{\text{Quick lime}}{CaO_{(s)}} + CO_2\uparrow$

$(vi) \quad \underset{\text{Calcium}}{2Ca_{(s)}} + O_{2(g)} \rightarrow \underset{\text{Calcium oxide}}{2CaO_{(s)}}$

31. Discuss briefly the similarities between beryllium and aluminium.
Diagonal relationship:
As observed in alkali metals, beryllium shows a diagonal relationship with aluminium.
Similarities between beryllium and aluminium:

1. Beryllium and aluminium have same electronegativity values.
2. Their changes per unit area is closer.
3. $BeCl_2$ and $AlCl_3$ forms dimeric structure. Both are soluble in organic solvents and are strong Lewis acids.
4. $Be(OH)_2$ and $Al(OH)_3$ dissolves in excess alkali to give beryllate ion $[Be(OH)_4]^{2-}$ and aluminate ion $[Al(OH)_4]^-$, respectively.
5. Be and Al ions have strong tendency to form complexes, e.g. BeF_4^{2-} and AlF_6^{3-}
6. Both $Be(OFI)_2$ and $Al(OH)_3$ are amphoteric in nature.
7. Carbide of Be – beryllium carbide (Be_2C) and Al – aluminium carbide (Al_4C_3) give methane on hydrolysis.
8. Both beryllium and aluminium are rendered passive by nitric acid.

32. Give the systematic names for the following:
1. **milk of magnesia**
2. **lye**
3. **lime**
4. **caustic potash**
5. **washing soda**

6. **soda ash and**
7. **trona.**
   Answer:
1. Milk of magnesia – $Mg(OH)_2$ – Magnesium hydroxide
2. Lye – $NaOH$ – Sodium hydroxide
3. Lime – $Ca(OH)_2$ Calcium hydroxide
4. Caustic potash – KOH – Potassium hydroxide
5. Washing soda – $Na_2CO_3. 10H_2O$ – Sodium carbonate decahydrate
6. Soda ash – Na_2CO_3 – Sodium carbonate (anhydrous)
7. Trona – $NaCO_3.NaHCO_3.2H_2O$ – Sodium sesqui carbonate

33. Substantiate lithium fluoride has the lowest solubility among group one metal fluorides.

Lithium fluoride has high lattice enthalpy due to the small size of Li^+ and F^- . So, due to the high lattice enthalpy, LiF is less soluble in water.

34. Mention the uses of Plaster of Paris.

- The largest use of Plaster of Paris is in the building industry as well as plasters.
- It is used for immobilizing the affected part of organ, where there is a bone fracture or sprain.
- It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

## 35. Beryllium halides are covalent whereas magnesium halides are ionic why?

Beryllium ion (Be^{2+}) is smaller in size and it is involved in equal sharing of electrons with halogens to form covalent bond, whereas magnesium ion (Mg^{2+}) is bigger and it is involved in transfer of electrons to form ionic bond.

36. Alkaline earth metal (A), belongs to 3rd period reacts with oxygen and nitrogen to form compound (B) and (C) respectively. It undergo metal displacement reaction with AgNO₃ solution to form compound (D).

1. An alkaline earth (A) metal belongs to third period is magnesium (Mg).
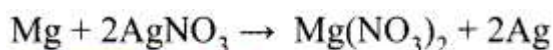2. Magnesium reacts with oxygen to form magnesium oxide (MgO) (B).

$$2Mg + O_2 \rightarrow 2MgO$$
$$\text{Magnesium oxide}$$
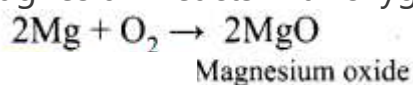
3. Magnesium reacts with nitrogen to form magnesium nitride Mg_3N_2 (C).

$$3Mg + N_2 \rightarrow Mg_3N_2$$
$$\text{Magnesium nitride}$$
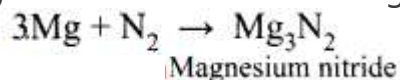
4. Magnesium undergoes metal displacement reaction with AgNO₃ solution to form magnesium nitrate $Mg(NO_3)_3$ (D).

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

<div align="center">Magnesium nitrate</div>

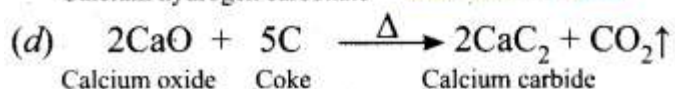| A	Magnesium	Mg
B	Magnesium oxide	MgO
C	Magnesium nitride	Mg_3N_2
D	Magnesium nitrate	$Mg(NO_3)_2$

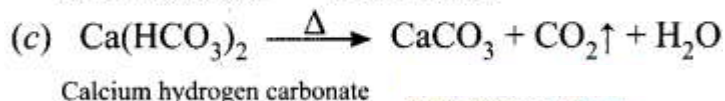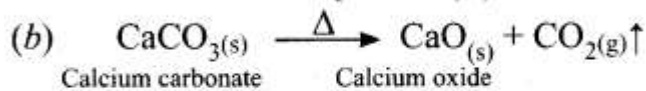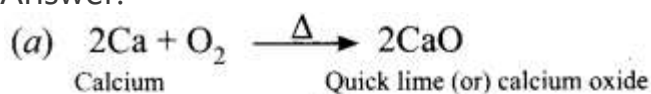**37. Write balanced chemical equation for the following processes:**

(a) heating calcium in oxygen

(b) heating calcium carbonate

(c) evaporating a solution of calcium hydrogen carbonate

(d) heating calcium oxide with carbon

Answer:

(a) $\underset{\text{Calcium}}{2Ca} + O_2 \xrightarrow{\Delta} \underset{\text{Quick lime (or) calcium oxide}}{2CaO}$

(b) $\underset{\text{Calcium carbonate}}{CaCO_{3(s)}} \xrightarrow{\Delta} \underset{\text{Calcium oxide}}{CaO_{(s)}} + CO_{2(g)}\uparrow$

(c) $\underset{\text{Calcium hydrogen carbonate}}{Ca(HCO_3)_2} \xrightarrow{\Delta} CaCO_3 + CO_2\uparrow + H_2O$

(d) $\underset{\text{Calcium oxide}}{2CaO} + \underset{\text{Coke}}{5C} \xrightarrow{\Delta} \underset{\text{Calcium carbide}}{2CaC_2} + CO_2\uparrow$

38. Explain the important common features of group 2 elements. Important common features of group 2 elements.

1. Group 2 elements except beryllium are commonly known as alkaline earth metals because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the Earth's crust.
2. Many alkaline earth metals are used in creating colours and used in fireworks.
3. Their general electronic configuration is ns^2.
4. Atomic and ionic radii of alkaline earth metals are smaller than alkali metals, on moving down the group, the radii increases.
5. These elements exhibit +2 oxidation state in their compounds.
6. Alkaline earth metals have higher ionizatoin enthalpy values than alkali metals and they are less electropositive than alkali metals.
7. Hydration enthalpies of alkaline earth metals decreases as we go down the group.
8. Electronegativity values of alkaline earth metals decrease down the group.
9. Alkaline earth metal salts moistened with concentrated hydrochloric acid gave a characteristic coloured flame, when heated on a platinum wire in a flame.

39. Discuss the similarities between beryllium and aluminium.

Diagonal relationship:

As observed in alkali metals, beryllium shows a diagonal relationship with aluminium. Similarities between beryllium and aluminium:

- Beryllium and aluminium have same electronegativity values.
- Their changes per unit area is closer.
- $BeCl_2$ and $AlCl_3$ forms dimeric structure. Both are soluble in organic solvents and are strong Lewis acids.
- $Be(OH)_2$ and $Al(OH)_3$ dissolves in excess alkali to give beryllate ion $[Be(OH)_4]^{2-}$ and aluminate ion $[Al(OH)_4]^-$, respectively.
- Be and Al ions have strong tendency to form complexes, e.g. BeF_4^{2-} and AlF_6^{3-}
- Both $Be(OFl)_2$ and $Al(OH)_3$ are amphoteric in nature.
- Carbide of Be – beryllium carbide (Be_2C) and Al – aluminium carbide (Al_4C_3) give methane on hydrolysis.
- Both beryllium and aluminium are rendered passive by nitric acid.

40. Why alkaline earth metals are harder than alkali metals?

1. The strength of metallic bond in alkaline earth metals is higher than alkali metals due to the presence of 2 electrons in its outermost shell as compared to alkali metals, which have only 1 electron in valence shell. Therefore, alkaline earth metals are harder than alkali metals.

2. The alkaline earth metals have greater nuclear charge and more valence electrons, thus metallic bonding is more effective. Due to this they are harder than alkali metals.

41. How is plaster of paris prepared?

Plaster of paris is a hemihydrate of calcium sulphate $CaSO_4$. H_2O. It is obtained by heating gypsum at 393 K.

$$2CaSO_4.2H_2O_{(s)} \xrightarrow{\Delta} 2CaSO_4.H_2O + 3H_2O$$

Gypsum   Plaster of paris
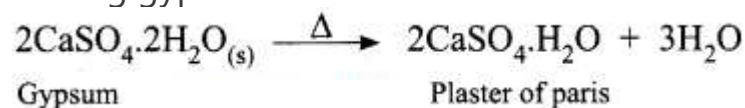
42. Give the uses of gypsum.

- The Alabaster variety of gypsum was used by the sculptors.
- Gypsum is used in making dry walls or plaster boards.
- Gypsum is used in the production of Plaster of Paris, which is used as a sculpting material
- Gypsum is used in making surgical and orthopedic casts.
- It plays an important role in agriculture as a soil additive, conditioner and fertilizer
- Gypsum is used in toothpaste, shampoo and hair products.
- Calcium sulphate acts as a coagulator in making tofu.
- It is also used in baking as a dough conditioner.
- Gypsum is a component of Portland cement, where it acts as a hardening retarder to control the speed at which concrete sets.
- Gypsum is used to give colour to cosmetics and drugs.
- Gypsum plays a very important role in wine making.

43. Describe briefly the biological importance of calcium and magnesium.

1. An adult body contains about 25 g of Mg and 1200 g of Ca. The daily requirement in the human body has been estimated to be 200-300 mg.
2. Magnesium is the co-factor of all enzymes that utilize ATP in phosphate transfer and energy release.
3. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium.
4. About 99% of body calcium is present in bones and teeth.
5. Calcium plays important roles in neuromuscular function, intemeuronal transmission, cell membrane integrity and blood coagulation.
6. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone.
7. Deficiency of magnesium results into convulsion and neuromuscular irritation.
8. 2% of adult weight is made up of calcium. Calcium phosphate is present in teeth and Calcium carbonate is present in bones. They make the teeth and bone hard.
9. Water in the human body such as inside the cell and in the blood contain dissolved calcium ions. These ions are involved in making muscles move and in sending electricity around the brain and along the nerves.
10. Magnesium is an essential element in both plant and animal life.

44. Which would you expect to have a higher melting point, magnesium oxide or magnesium fluoride? Explain your reasoning.

Magnesium oxide has very strong ionic bonds as compared to magnesium fluoride.
- Mg^{2+} and O^{2-} have charges of +2 and -2, respectively.
- Oxygen ion is smaller than fluoride ion.
- The smaller the ionic radii, the smaller the bond length in MgO and the bond is stronger than MgF_2.
- Due to more strong bond nature in MgO, it has high melting point than MgF_2.

UNIT 6 GASEOUS STATE

II. Answer these questions briefly.

26. State Boyle's law.

Boyle's law states that at a given temperature. the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

$V \alpha \frac{1}{P}$;

where T and n are fixed or PV = Constant = k

27. A balloon filled with air at room temperature and cooled to a much lower temperalure can be used as a model for Charles' law.

Charles' law:

- V T at constant P and n (or) $\frac{V}{T}$ = Constant
- A balloon filled with air at room temperature and cooled to a much lower temperature. the size of the balloon is reduced. Because if the temperature of the gas decreases, the volume also decreases in a direct proportion.
- When temperature is reduced, the gas molecules inside in over slower due to decreased temperature and hence the volume decreases.

28. Name two items that can serve as a model for Gay Lussac's law and explain.

Gay Lussac's law:

1. P α T at constant volume (or) = $\frac{V}{T}$

2. Example – 1:

You fill the car type completely full of air on the hottest day of summer. The type cannot change it shape and volume. But when winter comes, the pressure inside the lyre is reduced and the shape is also reduced. This confirms that pressure and temperature are direct related to each other.

3. Example – 2:

The egg in the bottle experiment.
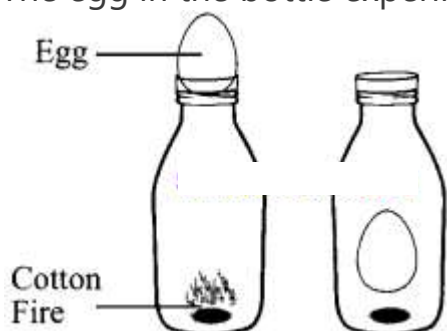
A glass bottle is taken, inside the bottle put some pieces of cotton with fire. Then place a boiled egg (shell removed) at the top of the bottle. The temperature inside the bottle increases from the fire, rising (he pressure. By scaling the bottle with egg, the fire goes on, dropping the temperature and pressure. This causes the egg to be sucked into the bottle.

P α T is proved (or) = $P_1V_1 = P_2V_2$

29. Give the mathematical expression that relates gas volume and moles. Describe in words what the mathematical expression means.

1. The mathematical relationship betwêen the volume of a gas and the number of moles is V α n
2. $V_1n_1=V_2n_2$ = Constant
   Where V_1 and n_1 are the volume and number of moles of a gas and V_2 and n_2 are the values of volume and number of moles of same gas at a different set of conditions.
3. If the volume of the gas increase then the number of moles of the gas also increases.
4. At a certain temperature and pressure, the volume of a gas is dirctly proportional to the number of the moles of the gas.

30. What are ideal gases? In what way real gases differ from ideal gases.

1. Ideal gases are the gases that obey gas laws or gas equation PV = nRT.
2. Real gases do not obey gas equation. PV = nRT.
3. The deviation of real gases from ideal behaviour is measure in terms of a ratio of PV to nRT. This is termed as compression factor (Z). $Z = \frac{PV}{nRT}$
4. For ideal gases Z = 1.
5. For real gases Z > 1 or Z < 1. For example, at high pressure real gases have Z >1 and at intermediate pressure Z < 1.
6. Above the Boyle point Z> 1 for real gases and below the Boyle point, the real gases first show a decrease for Z, reaches a minimum and then increases with the increase in pressure.
7. So, it is clear that at low pressure and high temperature, the real gases behave as ideal gases.

31. Can a Van der Waals gas with a = 0 be liquefied? Explain.

- a = 0 for a Van der Waals gas i.e. for a real gas. Van der Waals constant a = 0. It cannot be liquefied.
- If a = 0, there is a very less interaction between the molecules of gas.
- 'a' is the measure of strength of Van der Waals force of attraction between the molecules of the gas.
- If a is equal to zero, the Van der Waals force of attraction is very less and the gas cannot be liquefied.

32. Suppose there ¡s a tiny sticky area on the wan of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary area of walls?

- Molecules hitting the tiny sticky area on the wall of the container of gas moves faster as they get closer to adhesive surface, but this effect is not permanent.
- The pressure on the sticky wall is greater than on the ordinary area of walls.

33.Explain the following observations
(a) Aerated water bottles are kept under water during summer
(b) Liquid ammonia bottle is cooled before opening the seal
(c) The type of an automobile is inflated to slightly lesser pressure in summer than in winter
(d) The size of a weather balloon becomes larger and larger as it ascends up into larger altitude

(a) In aerated water bottles, CO_2 gas is passed through the aqueous solution under pressure because the solubility of the gas in water is not very high. In summer, the solubility of the gas in water is likely to decrease because of the rise in temperature. Thus, in summer, more of gas will be present above the liquid surface in the glass bottle.

In case, the pressure of the gas becomes too high, the glass will not be able to withstand the pressure and the bottle may explode. To avoid this, the bottles are kept under water. As a result, the temperature is likely to decrease and the solubility of CO_2 is likely to increase in aqueous solution resulting in decreased pressure.

(b) Liquid ammonia bottle contains the gas under very high pressure. If the bottle is opened as such, then the sudden decrease in pressure will lead to a large increase in volume of the gas. As a result, the gas will come out of the bottle all of a sudden with force. This will lead to the breakage of the bottle and also causes accident.

However, if the bottle is cooled under tap water for sometime, there will be a decrease in the volume of a gas to a large extent. if the seal is opened now, the gas will corne out of the bottle at a slower rate, reduces the chances of accident.

(c) The pressure of air is directly proportional to the temperature. Since the temperature is higher in summer than in higher, the pressure of the air in the tube of the lyre is likely to be quite high as compared to winter. It is quite likely that the tube may burst under high pressure in summer, Therefore, it is advisable to inflate the types to lesser pressure in summer than in winter.

(d) The volume of the gas is inversely proportional to pressure at a given temperature according to Boyle's law. As the weather balloon ascends, the pressure tends to decrease. As a result, the volume of the gas inside the balloon or the size of the balloon is likely to increase.

34.Give suitable explanation for the following facts about gases.
(a) Gases don't settle at the bottom of a container
(b) Gases diffuse through all the space available to them and
(c) Explain with an increase in temperature

(a) Gases by definition are the least dense state of matter. They have negligible intermolecular forces of attraction. So they are all free to roam separately. So the least dense gas particles will not sink at the bottom of a container.

(b) When a sample of a gas introduced to one part of a closed container, its molecules very quickly disperse throughout the container, this process by which molecules

disperse in space in response to differences in concentration is called diffusion. For e.g., you can smell perfume in a room, because it difluses into the air totally inside the room.

(c) Diffusion is faster at higher temperature because the gas molecules have greater kinetic energy. Since heat increase the motion, then diffusion happens faster.

35. Suggest why there ¡s no hydrogen (H_2) in our atmosphere. Why does the moon have no atmosphere?

1. Hydrogen is the lightest element thus when produced in free state, it rises above all the other gases to the top of the atmosphere, where it is open to cosmic storms and solar flares. There it literally leaks from the atmosphere to the empty space. Hydrogen easily gains velocity required to escape Earth's magnetic field. Hydrogen is very reactive in nature. So it would have reacted with O_2, in its way to produce H_2O. So majority portion of H_2 reacts and very less amount of it present in the upper level of atmosphere and gains velocity to escape the atmosphere.

2. Moon has no atmosphere because the value of acceleration due to gravity 'g' on the surface of the moon is small. Therefore, the value of escape velocity on the surface of the moon is very small. The molecule of the atmospheric gases on the surface of the moon have thermal velocities greater than the escape velocity. That's why all the molecules of gases have escaped and there is no atmosphere in the moon. The moon has insufficient gravity to retain an atmosphere. So we conclude that moon has no atmosphere.

36. Explain whether a gas approaches ideal behaviour or deviates from ideal behaviour if –
(a) it is compressed to a smaller volume at constant temperature
(b) the temperature is raised while keeping the volume constant
(c) more gas is introduced into the same volume and at the same temperature

(a) it a gas is compressed to a smaller volume at constant temperature, pressure is increased. At high pressure with a smaller volume, the gas deviates from ideal behaviour.

(b) If a gas temperature is raised keeping the volume constant, the pressure of the gas will increase. At high pressure, the gas deviates from ideal behaviour.

(c) if more gas is introduced into the same volume and at the same temperature, the number of moles are increasing. if the volume remains same, the increased number of moles collide with each other and kinetic energy increases and pressure decreases. At increased pressure, the gas deviates from ideal behaviour.

37. Which of the following gases would you expect to deviate from ¡deal behaviour under conditions of low temperature F Cl_2, or Br_2? Explain.

1. Bromine deviates (Br_2) from the ideal gas maximum than Cl_2 and F_2. Because Br_2 has biggest size (atomic weight 79.9) provides maximum attraction between bromine molecules which is directly proportional to the size of the molecule and the boiling point of the liquid made from those molecules.

2. Br_2 deviates from ideal behaviour because it has largest atomic radii compared to Cl_2 and F_2. So it contains more electrons than other two, and the Vander Waals forces are stronger in Br_2 than in Cl_2 and F_2. So Br_2 deviates from ideal behaviour.

38. Distinguish between diffusion and effusion.

Diffusion:
- Diffusion is the spreading of molecules of a substance throughout a space or a second substance.
- Diffusion refers to the ability of the gases to mix with each other.
- E.g.. Spreading of something such as brown tea liquid spreading through the water in a tea cup.

Effusion:
- Effusion is the escape of gas molecules through a very small hole in a membrane into an evacuated area.
- Effusion is a ability of a gas to travel through a small pin-hole.
- E.g., pouring out something like the soap studs bubbling out from a bucket of water.

39. Aerosol cans carry clear warning of heating of the can. Why?

Aerosol cans carry clear warning of heating of the can. As the temperature rises, pressure in the can will increase and ambient temperatures about 120°F may lead to explosions. So aerosol cans should always be stored in dry areas where they will not be exposed to excessive temperatures. You should never throw an aerosol can onto a fire or leave it in the direct sunlight. even it is empty. This is because the pressure will build up so much that the can will burst. It is due to 2 reasons.
- The gas pressure increases.
- More of the liquefied propellant turns into a gas.

40. When the driver of an automobile applies brake, the passengers are pushed toward the front of the car but a helium balloon is pushed toward back of the car. Upon forward acceleration the passengers are pushed toward the front of the car. Why?

1. When the driver of an automobile applies brake, the passengers are pushed toward the front of the car due to inertia of the body, but a helium balloon pushed toward back of the car. Helium balloon responds to the air around it. Helium molecules are lighter than air of our atmosphere, and so they move toward back by gravity as a result of the accelerating frame.

2. Upon forward acceleration, the passengers arc pushed toward the front of the car, because the body in motion tends to stay in motion until acted upon by an outside force. Helium balloon is going to move opposite to this pseudo gravitational force.

41. Would it be easier to drink water with a straw on the top of Mount Everest?

It is difficult to drink water with a straw on the top of Mount Everest. This is because the reduced atmospheric pressure is less effective in pushing water into the straw at the top

of the mountain because gravity falls off gradually with height. The air pressure falls off, there isn't enough atmospheric pressure to push the water up in the straw all the way to the mouth.

42. Write the Van der Waals equation for a real gas. Explain the correction term for pressure and volume.

Van der Waals equation of state for real gases is –

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

Correction term for pressure:

$\frac{an^2}{V^2}$ is the pressure correction. It represents the intermolecular interaction that causes the non ideal behaviour.

Correction term for Volume:

V – nb is the volume correction. it is the effective volume occupied by real gas.

43. Derive the values of critical constants from the Van der Waals constants.

Derivation of critical constants from the Van der Waals constants:

Van der Waals equation is,

$\left(P + \frac{an^2}{V^2}\right)(V - nb)$ = nRT for 1 mole

From this equation, the values of critical constant $P_C V_C$ and T_C arc derived in terms of a and b the Van der Waals constants.

$\left(P + \frac{an^2}{V^2}\right)(V - b)$ = RT ....(1)

On expanding the equstion (1)

P V + $\frac{a}{V}$ – pb – $\frac{ab}{V^2}$ – RT = 0 ....(2)

Multiplying eqestion (2) by $\frac{V^2}{P}$,

$\frac{V^2}{P}\left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT\right) = 0$

$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0$ ......(3)

equation (3) is rearranged in the powers of V

$V^3 - \left[\frac{RT}{P} + b\right]V^2 + \frac{aV}{P} -$

= 0 ....(4)

The above equation (4) is an cubic equation of V, which can have three roots. At the critical point. all the three values of V are equal to the critical volume V_C.

i.e. V = V_C.

V – V_C = O ....(5)

$(V - V_C)^3 = 0 \ldots\ldots(6)$

$(V^3 - 3V_CV^2 + 3V_C^3V - V_C^3 = 0 \ldots\ldots(7)$

As the equation (4) is identical with equation (7), comparing the 'V' ternis in (4) and (7),

$$-3V_CV^2 = -\left[\frac{RT_C}{P_C} + b\right]V^2 \quad \ldots\ldots(8)$$

$$3V_C = b + \frac{RT_C}{P_C} \quad \ldots\ldots(9)$$

$$3V_C^2 = \frac{a}{P_C} \quad \ldots\ldots(10)$$

$$V_C^3 = \frac{ab}{P_C} \quad \ldots\ldots(11)$$

Divide equation (11) by (10)

$$\frac{V_C^3}{3V_C^2} = \frac{ab/P_C}{a/P_C}$$

$$\frac{V_C}{3} = b$$

$$\therefore V_C = 3b \quad \ldots\ldots(12)$$

When equation (12) is substituted in (10)

$$3V_C^2 = \frac{a}{P_C}$$

$$P_C = \frac{a}{3V_C^2} = \frac{a}{3(3b)^2} = \frac{a}{3 \times 9b^2} = \frac{a}{27b}$$

$$\therefore P_C = \frac{a}{27b^2} \quad \ldots\ldots(13)$$

substituting the values of Vc and Pc in equation (9)

$$3V_C = b + \frac{RT_C}{P_C}$$

$$3 \times 3b = b + \frac{RT_C}{a/27b^2}$$

$$9b - b = \frac{RT_C}{a} \times 27b^2$$

$$8b = \frac{T_C \cdot R 27b^2}{a}$$

$$\therefore T_C = \frac{8ab}{27Rb^2} = \frac{8a}{27Rb}$$

$$T_C = \frac{8a}{27Rb} \quad \ldots\ldots(14)$$

Critical constant a and b can be calculated using Van der Waals Constant as follows:

$$a = 3V_C^2 P_C$$

$$b = \frac{V_C}{3}$$

..........(15)

44. Why do astronauts have to wear protective suits when they are on the surface of moon?

In space, there is no pressure, if we do wear a pressurised suit, our body will die. In space, we have to wear a pressurised suit, otherwise our body will continue to push out and blow up like a balloon. It would look cool, but we will be dead. So the astronauts in space must wear a pressurised suit (protective suits).

45.When ammonia combines with HCl, NH₄ Cl is formed as white dense fumes. Why do more funies appear near HCl?

1. When ammonia combines with HCl, NH_4 Cl is formed as white dense fumes. The reaction takes place in neutralization between a weak base and a strong acid.
2. The property of the gas is diffusion.
3. Diffusion of gases Ammonia and hydrogen chloride. Concentrated ammonia solution is placed on a pad in one end of a tube and concentrated HCl on the pad at the other. After about a minute, the gases diffuses far enough to meet and a ring of solid ammonium chloride is formed near the HCl end.

46. A sample of gas at 15°C at 1 atm has a volume of 2.58 dm³. Vhen the temperature is raised to 38°C at I atm does the volume of the gas increase? if so, calculate the final volume.

Answer:

$$T_1 = 15°C + 273 \qquad T_2 = 38°C + 273$$
$$T_1 = 288 \text{ K} \qquad\quad T_2 = 311 \text{ K}$$
$$V_1 = 2.58 \text{ dm}^3 \qquad V_2 = ?$$
(P = 1 atom constant)
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$V_2 = \left(\frac{V_1}{T_1}\right) \times T_2$$
$$= \frac{2.58 \text{ dm}^3}{288 \cancel{K}} \times 311 \cancel{K}$$

V_2 = 2.78 dm³ i.e. volume increased from 2.58 dm³ to 2.78 dm³.

47. A sample of gas has a volume of 8.5 dm³ at an unknown temperature. When the sample is submerged in ice water at 0°C, its volume gets reduced to 6.37 dm³. What ¡s its initial temperature?

Answer:

$$V_1 = 8.5 \text{ dm}^3 \qquad V_2 = 6.37 \text{ dm}^3$$
$$T_1 = ? \qquad T_2 = 0°C = 273 \text{ K}$$
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$V_1 \times \left(\frac{T_2}{V_2}\right) = T_1$$
$$T_1 = 8.5 \text{ dm}^3 \times \frac{273 \text{ K}}{6.37 \text{ dm}^3}$$

T₁ = 364.28 K

48. Of two samples of nitrogen gas, sample A contains 1.5 moles of nitrogen in a vessel of volume of 37.6 dm³ at 298K, and the sample B is in a vessel of volume 16.5 dm³ at 298 K. Calculate the number of moles in sample B.

n_A = 1.5 mol n_B = ?

V_A = 37.6 dm³ V_B = 16.5 dm³

(T = 298 K constant)

$$\frac{V_A}{n_A} = \frac{V_B}{n_B}$$

$$n_A = \left(\frac{n_A}{V_A}\right)V_B$$

$$= \frac{1.5 \text{ mol}}{37.6 \text{ dm}^3} \times 16.5 \text{ dm}^3$$

49. Sulphur hexafluoride is a colourless, odourless gas; calculate the pressure exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 dm³ at 69.5°C, assuming ¡deal gas behaviour.

n = 1.82 mole

V = 5.43 dm³

T = 69.5 + 273 = 342.5

P = ?

PV = nRT

$P = nRTV$

$$P = \frac{1.82 \text{ mol} \times 0.821 \text{ dm}^3 \text{ atm mol}^{-1}\text{K}^{-1} \times 342.5 \text{ K}}{5.43 \text{ dm}^3}$$

P = 94.25 atm.

50. Argon is an inert gas used in light bulbs to retard the vapourlzation of the tungsten filament. A certain light bulb containing argon at 1.2 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure in atm.

Answer:

P₁ = 1.2 atm

T₁ = 18°C + 273 = 291 K

T₂ = 85°C + 273 = 358 K

$P_2 = ?$

$P_1T_1 = P_2T_2$

$$P_2 = \left(\frac{P_1}{T_1}\right) \times T_2$$

$$= \frac{1.2 \text{ atm}}{291 \text{ K}} \times 358 \text{ K}$$

51. A small bubble rises from the bottom of a lake, where the temperature and pressure are 6°C and 4 atm. to the water surface, where the temperature is 25°C and pressure is 1 atm. Calculate the final volume in (mL) of the bubble, if its initial volume is 1.5 mL.

$T_1 = 6°C + 273 = 279$ K

$P_1 = 4$ atm $V_1 = 1.5$m

$T_2 = 25°C + 273 = 298$ K

$P_2 = 1$ atm $V_1 = ?$

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

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{4 \text{ atm} \times 1.5 \text{ ml} \times 298 \text{ K}}{279 \text{ K} \times 1 \text{ atm}}$$

$V_2 = 6.41$ mol.

52. Hydrochloric acid is treated with a metal to produce hydrogen gas. Suppose a student carries out this reaction and collects a volume of 154.4 x 10⁻³ dm³ of a gas at a pressure of 742 mm of Hg at a temperature of 298 K. What mass of hydrogen gas (in mg) did the student collect?

$V = 154.4 \times 10^{-3} \text{dm}^3$

$P = 742$ mm of Hg

$T = 298$ K $m = ?$

$$n = \frac{PV}{RT} =$$

$$= \frac{742 \text{ mm Hg} \times 154.4 \times 10^{-3} \text{L}}{62 \text{ mm Hg L K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}$$

$= 0.006$ mol

$$n = \frac{PV}{RT}$$

$$n = \frac{Mass}{MolarMass}$$

$Mass = n \times Molar\ mass$

$= 0.006 \times 2.016$

$= 0.0121$ g $= 12.1$ mg.

53. It takes 192 sec for an unknown gas to diffuse through a porous wall and 84 sec for N2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

Answer:

$$\frac{\gamma_{unknown}}{\gamma_{N_2}} = \frac{t_{N_2}}{t_{unknown}} = \sqrt{\frac{m_{N_2}}{m_{unknown}}}$$

$$\frac{84\,sec}{192\,sec} = \sqrt{\frac{14g\ mol^{-1}}{m_{unknown}}}$$

$$= \frac{14g\ mol^{-1}}{m_{unknown}}$$

$$m_{unknown} = 14g\ mol^{-1} \times \left(\frac{192\,sec}{84\,sec}\right)^2$$

$$m_{unknown} = 73.14\ g\ mol^{-1}$$

54. A tank contains a mixture of 52.5 g of oxygen and 65.1 g of CO2 at 300 K the total pressure in the tank ¡s 9.21 atm. Calculate the partial pressure (in atm.) of each gas in the mixture.

Answer:

m_{O_2} = 52.5 g

P_{O_2} = ?

m_{CO_2} = 65.1 g

P_{CO_2} = ?

T = 300 K   P = 9.21 atm

$P_{O_2} = X_{O_2} \times$ total pressure

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{CO_2}}$$

$$n_{O_2} = \frac{\text{Mass of } O_2}{\text{Molar mass of } O_2}$$

$$= \frac{52.5\ g}{32\ g\ mol^{-1}} = 1.64\ mol$$

$$n_{CO_2} = \frac{\text{Mass of } CO_2}{\text{Molar mass of } CO_2}$$

$$= \frac{65.1\ g}{44\ g\ mol^{-1}} = 1.48\ mol$$

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{CO_2}} = \frac{1.64}{3.12} = 0.53$$

$$X_{CO_2} = \frac{n_{CO_2}}{n_{O_2} + n_{CO_2}} = \frac{1.48}{3.12} = 0.47$$

P_{O_2} = X_{O_2} x Total pressure

= 0.53 x 9.21 atm = 4.88 atm

P_{CO_2} = X_{CO_2} x Total pressure

= 0.47 x 9.21 atm = 4.33 atm

55. A combustible gas Is stored in a metal tank at a pressure of 2.98 atm at 25 °C. The tank can withstand a maximum pressure of 12 atm after which it will explode. The building in which the tank has been stored catches fire. Now predict whether the tank will blow up first or start melting? (Melting point of the metal = 1100 K).

T_1 = 298 K;

P_1 = 2.98 atm;

T_2 = 1100K;

P_2 = ?

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = \frac{P_1}{T_1} \times T_2$$

= 2.98atm 298K×1100K = 11 atm

At 1100 K, the pressure of the gas inside the tank will become 11 atm. Given that tank can withstand a maximum pressure of 12 atm, the tank will start melting first.

II . Answer these questions briefly.

26. State the first law of thermodynamics.

The first law of thermodynamics states that "the total energy of an isolated system remains constant though it may change from one form to another"

(or)

Energy can neither be created nor destroyed, but may be converted from one form to another.

27. Define Hess's law of constant heat summation.

Hess's law:

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps.
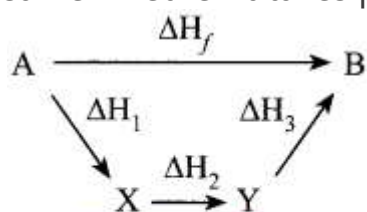
$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3$$

28. Explain intensive properties with two examples.

The property that is independent of the mass or size of the system is called as intensive property.

e.g., Refractive index and surface tension.

29. Define the following terms:

(a) isothermal process

(b) adiabatic process

(c) isobaric process

(d) isochoric process

Answer:

(a) isothermal process:

It is defined as one in which the temperature of the system remains constant, during the change from its initial to final states.

(b) Adiabatic process:

It is def'ined as one in which there is no exchange of heat (q) between the system and surrounding during operations.

(c) Isobaric process:

It is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

(d) Isochoric process:
It is defined as one in which the volume of system remains constant during its change from initial to final state of the process.

30. What is the usual definition of entropy? What is the unit of entropy?
Entropy is a thermodynamic state function that is a measure of the randomness or disorderliness of the system.

1. For a reversible change taking place at a constant temperature (T). the change in entropy
2. of the system is equal to heat energy absorbed or evolved (q) by the system divided by the constant temperature (T).

$$\Delta S_{sys} = \frac{q_{rev}}{T}$$

3. SI unit of entropy is J K^{-1}

31. Predict the feasibility of a reaction when
1. **both ΔH and ΔS positive**
2. **both ΔH and ΔS negative**
3. **AH decreases but ΔS increases**
   Answer:
1. When both ΔH and ΔS are positive, the reaction is not feasible.
2. When both ΔH and ΔS are negative, the reaction is not feasible.
3. When ΔH decreases but ΔS increases, the reaction is feasible.

32. Define Gibb's free energy.
Gibbs free energy is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

G = H -TS,
where G = Gibb's free energy
H = enthalpy
T = temperature
S = entropy

33. Define enthalpy of combustion.
Enthalpy of combustion of a substance is defined as "the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen". it is denoted as ΔH.

34. Define molar heat capacity. Give its unit.
Molar heat capacity is defined as "the amount of heat absorbed by one mole of a substance in raising the temperature by I Kelvin". It is denoted as C_m
Unit of Molar heat capacity: SI unit of C_m is $JK^{-1} mol^{-1}$.

35. Define the calorific value of food. What is the unit of calorific value?
- The calorific value of food is defined as the amount of heat produced in calories (or Joules) when one gram of food is completely burnt.
- Unit of calorific value (a) Cal g^{-1} (b) J Kg^{-1}

36. Define enthalpy of neutralization.

The enthalpy of neutralization is defined as the change in enthalpy of the system when one gram equivalent of an acid is neutralized by one gram equivalent of a base or vice versa in dilute solution.

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ = 57.32 kJ.
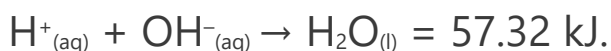
37. What is lattice energy?

Lattice energy is defined as the amount of energy required to completely separate one mole of a solid ionic compound into gaseous constituent.

38. What are state and path functions? Give two examples.

- The variables like P. V, T and 'n' that are used to describe the state of the system are called as state functions. e.g.. pressure, volume, temperature, internal energy, enthalpy and free energy.
- A path function is a thermodynamic property of the system whose value depends on the path or manner by which the system goes from its initial to final state. e.g., work (w) and heat (q).

39. Give Kelvin statement of second law of thermodynamics.

Kelvin-Planck statement:

It is impossible to take heat from a hotter reservoir and convert a cyclic process heat to a cooler reservoir.

40. The equilibrium constant of a reaction is 10, what will be the sign of ΔG? Will this reaction be spontaneous?

$\Delta G° = -2.303 \, RT \log K_{eq}$

$K_{eq} = 10$

$\therefore \Delta G° = -ve$ value.

So the reaction will be spontaneous.

41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

1. Enthalpy of neutralization of a strong acid by a strong base is always a constant and it is equal to -57.32 kJ irrespective of which acid or base is used.
2. Because strong acid or strong base means it is completely ionized in solution state. For e.g., NaOH (strong base) is neutralized by HCl (strong acid), due to their complete ionization, the net reaction take place is only water formation.

So the enthalpy of neutralization is always constant for strong acid by a strong base.
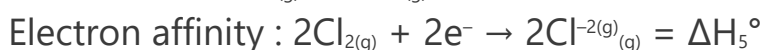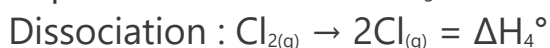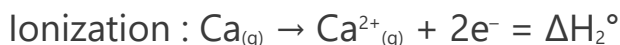
$H^+Cl^- + Na^+OH^- \rightarrow Na^+Cl^- + H_2O$

$H^+NO_3^+ + K^+OH^- \rightarrow K^+NO_3^+ + H_2O$

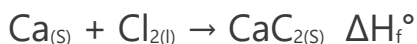(Net reaction) $H^+ + OH^- \rightarrow H_2O$ ΔH = -57.32 kJ
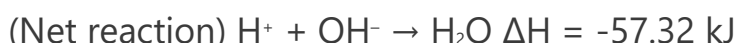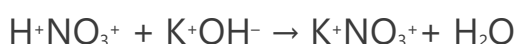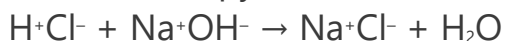
42. State the third law of thermodynamics.

It states that the entropy of pure crystalline substance at absolute zero is zero. (or)

It can be stated as "it is impossible to lower the temperature of an object to absolute zero in a finite number of steps". Mathematically $\lim\limits_{T \to 0} S = 1$

43. Write down the Born-Haber cycle for the formation of CaCl₂

Born – Haber cycle for the formation of CaCl₂

$Ca_{(S)} + Cl_{2(l)} \rightarrow CaC_{2(S)}$ $\Delta H_f°$

Sublimation : $Ca_{(S)} \rightarrow Ca_{(S)}$ $\Delta H_1°$

Ionization : $Ca_{(g)} \rightarrow Ca^{2+}{}_{(g)} + 2e^- = \Delta H_2°$

Vapourisation : $Cl_{2(l)} \rightarrow Cl_{2(g)} = \Delta H_3°$

Dissociation : $Cl_{2(g)} \rightarrow 2Cl_{(g)} = \Delta H_4°$

Electron affinity : $2Cl_{2(g)} + 2e^- \rightarrow 2Cl^{-2(g)}{}_{(g)} = \Delta H_5°$

Lattice enthalpy : $Ca^{2+}{}_{(g)} + 2Cl^-{}_{(g)} \rightarrow CaCl_{2(S)} = \Delta H_6°$
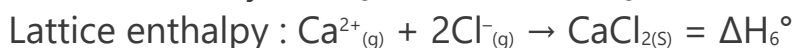
$\Delta H_f° = \Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4° + \Delta H_5° + \Delta H_6°$

44. Identify the state and path functions out of the following

(a) Enthalpy
(b) Entropy
(c) Heat
(d) Temperature
(e) Work
(f) Free energy.

State function : Enthalpy, entropy, temperature and free energy.
Path function : Heat and work.

45. State the various statements of second law of thermodynamics.

1. Entropy statement:
Whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe".

2. Kelvin-Planck statement:
it is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

3. Efficiency statement:
Even an ideal, frictionless engine cannot convert 100% of its input heat into work.

$$\text{Efficiency} = \frac{T_1 - T_2}{T_1}$$

$$\% \text{ Efficiency} = \left[\frac{T_1 - T_2}{T_1}\right] \times 100$$

$$\% \text{Efficiency} = \left[\frac{\text{Output}}{\text{Input}}\right] \times 100$$

$$\% \text{Efficiency} < 100\%$$

4. Clausius statement:
Heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to spend some work.

46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?

1. A reaction that does occur under the given set of conditions is called a spontaneous reaction.
2. The expansion of a gas into a evacuated bulb is a spontaneous process, the reverse process that is gathering of all molecules into one bulb is not spontaneous. This example shows that processes that occur spontaneously in one direction cannot take place in opposite direction spontaneously.
3. Increase in randomness favours a spontaneous change.
4. If enthalpy change of a process is negative, then the process is exothermic and occurs spontaneously. Therefore ΔH should be negative.
5. if entropy change of a process is positive, then the process occurs spontaneously, therefore ΔS should be positive.
6. If free energy of a process is negative, then the process occurs spontaneously, therefore ΔG should be negative.
7. For a spontaneous. irreversible process. $\Delta H < 0$, $\Delta S > 0$, $\Delta G < 0$. i.e., $\Delta H =$ -ve, $\Delta S =$ +ve and $\Delta G =$ -ve.

47. List the characteristics of internal energy.

- Internal energy of a system is an extensive property. It depends on the amount of the substances present in the system.
- Internal energy of a system is a state function. It depends only upon the state variables (T, P, V. n) of the system.
- The change in internal energy is as $\Delta U = U_2 - U_1$
- In a cyclic process, there is no energy change. $\Delta U_{(cyclic)} = 0$.
- If the internal energy of the system at final state (U_f) is less than the internal energy of the system at its initial state (U_i), then ΔU would be negative.
- if $U_f < U_i$ $\Delta U = U_f - U_i =$ -ve
  if $U_f > U_i$ $\Delta U = U_f - U_i =$ +ve

48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.

1. For chemical reactions, heal absorbed at constant volume, is measured in a bomb calorimeter.
2. Description of the apparatus and procedure:
The inner vessel and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws. A weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle

combustion. The bomb is then tightly closed and pressurizcd with excess

$$P_{ext} = \frac{\text{Force (F)}}{\text{Area (A)}} \quad \text{............(2)}$$

oxygen. The bomb is lowered in water, which is placed inside the calorimeter. A stirreris placed in the bomb to stir the water uniformly. The reaction is started by striking the substance through electrical heating.

3. During burning, the exothermic heat generated inside the bomb raises the temperature of the surrounding water bath. Temperature change can be measured accurately using Beckmann thermometer. Since the bomb calorimeter is sealed, its volume does not change, so the heat measurements in this case corresponds to the heat of reaction at constant volume.
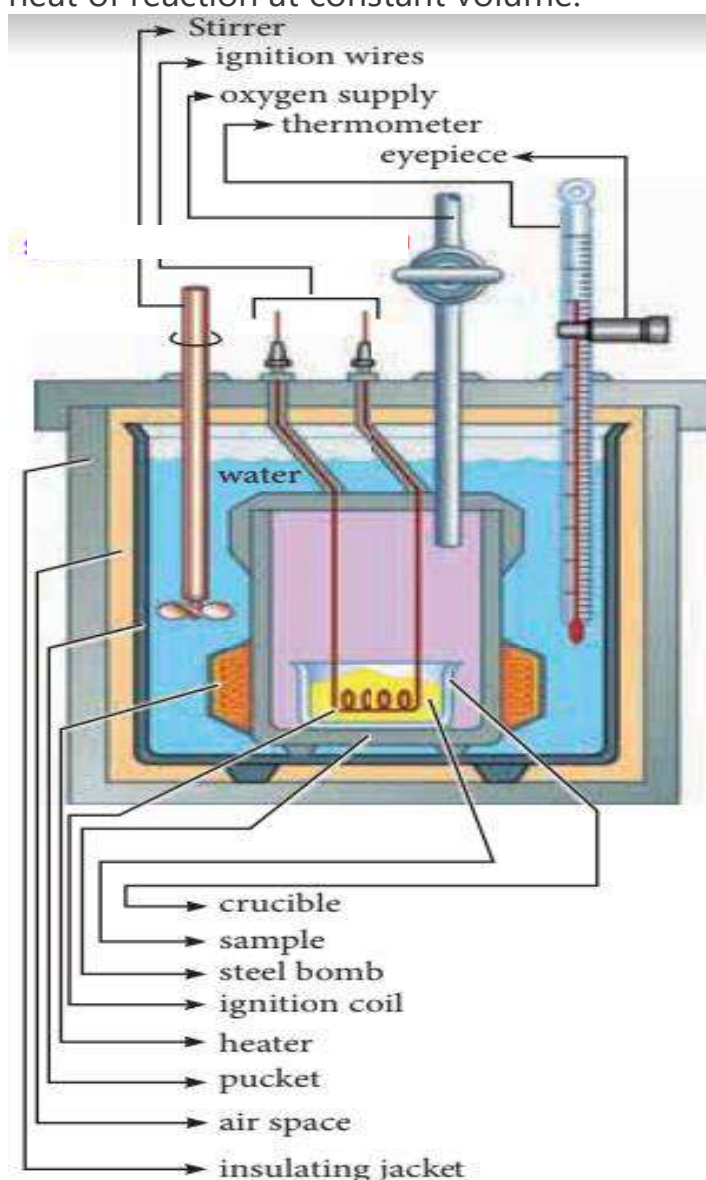
Bomb calorimeter

4. In a bomb calorimeter experiment, a weighed sample of benzoic acid (w) is placed in the bomb which is then filled with excess oxygen and sealed. Ignition is brought about electrically. The rise in temperature (AT) is noted. Water equivalent or calorimetry equivalent of the calorimeter is known from the standard value of enthalpy of combustion of benzoic acid.

5. $\Delta H_c(C_6H_5COOH) = -3227$ kJ mol^{-1}

$$\omega_e = \frac{\Delta H_C(C_6H_5COOH)}{\Delta T} \times \frac{W}{M_2}$$

6. By knowing o value, the enthalpy of combustion of any other substance is determined adopting the similar procedure and using the substance in place of' benzoic acid. By this experiment, the enthalpy of combustion at constant volume ($\Delta U_c°$) is known,

$\Delta U_c° = \omega_e. \Delta T$

7. Enthalpy of combustion at constant pressure of the substance is calculated from the equation

$\Delta U°_{C(pressure)} = \Delta U°_{C(volume)} + \Delta n_g$ RT

49. Calculate the work involved in expansion and compression process.

1. The essential condition of expansion or compression of a system is, there should be difference between external pressure P_{ext} and internal pressure (P_{int}).

2. If the volume of the system is increased against the external pressure. the work is done by the system. By convention work done by the system is given a negative sign (-w).
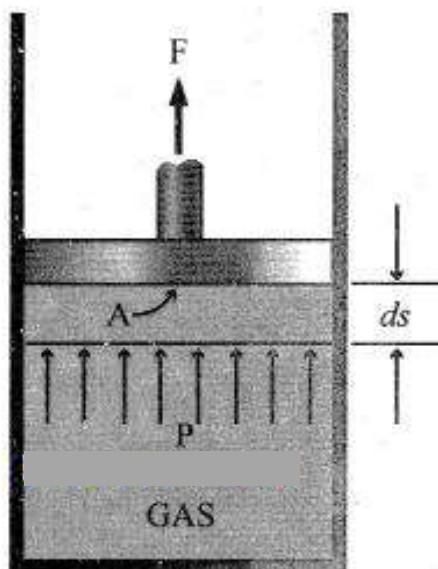
3. If the volume of the system decreased, the work is done on the system. By convention work done on the system is given a positive sign (+w).

4. For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is P_{int}.

5. If external pressure is P_{ext} which is greater than P_{int} piston is moved inward till the pressure inside becomes equal to P_{int} It is achieved in a single step and the final volume be V_f.

6. During this compression, piston moves a distance x) and is cross-sectional area of the piston is A, then, Change in volume = x A = $\Delta V = V_f - V_i$ ....(1)

$P_{ext} = \text{Force(F)Area(A)}$ ....(2)

$F = P_{ext}.A$

7. if work is done by the system by pushing out the piston against external pressure (P_{ext}) then according to the equation,

$-w = F.x$ ....(3)

$-w = P_{ext} . A . x$ ....(4)

$-w = P_{ext}.\Delta V$ ....(5)

$-w = P_{ext} . (V_f - V_i.)$ .....(6)

Simply $w = -P\Delta V$ ....(7)

8. From the above equation, we can predict the sign of work (w).

9. During expansion, work is done by the system, since $V_f > V_i$ the sign obtained for work will be negative.

10. During compression, work is done on the system, since $V_f < V_i$ the sign obtained for work will be positive.

50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

1. When the system at constant pressure undergoes changes from an initial state with H_1, U_1, V_1 and P parameters to a final state with H_2, U_2, V_2 and P parameters, the change in enthalpy ΔH, is given by

AH = U + PV

2. At initial state $H_1 = U_1 + PV_1$ ....(1)

At final state $H_1 = U_1 + PV_1$ ....(2)

(2) − (1) ⇒ $(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$

$\Delta H = \Delta U + P\Delta V$ ....(3)

Considering $\Delta U = q + w$; $w = -P\Delta V$

$\Delta H = q + w + P\Delta V$

$\Delta H = q_p - P\Delta V + P\Delta V$

$\Delta H = q_p$ ....(4)

q_p is the heat absorbed at constant pressure and is considered as heat content.

3. Consider a closed system of gases which are chemically reacting to produce product gases at constant temperature and pressure with V. and as the total volumes of the reactant and product gases respectively, and n1 and n_f are the number of moles of gaseous reactants
and products. Then,

For reactants: $P V_i = n_i RT$

For products: $P V_f = n_f RT$

Then considering reactants as initial state and products as final state,

$P (V_i - V_i) = (n_i - n_i) RT$

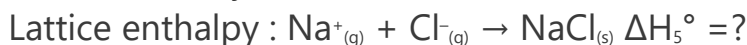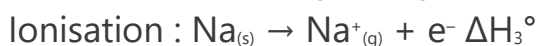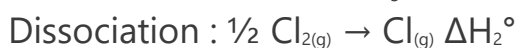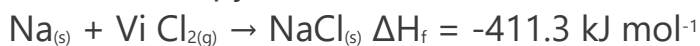$P\Delta V = \Delta n_g RT$

$\Delta H = \Delta U + P\Delta V$

$\Delta H = \Delta U + \Delta n_g \, RT$ ....(5)

51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.

The Born – Haber cycle is used to determine the lattice enthalpy of NaCl as follows:
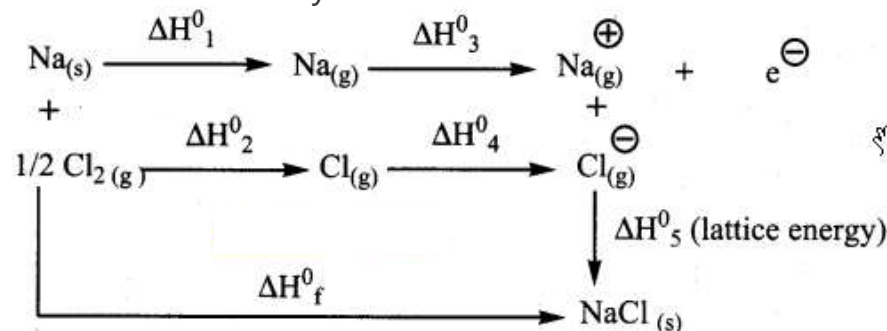
Formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

$Na_{(s)} + \text{Vi} \, Cl_{2(g)} \rightarrow NaCl_{(s)}$ $\Delta H_f = -411.3$ kJ mol^{-1}

Sublimation : $Na_{(s)} \rightarrow Na_{(g)}$ $\Delta H_1°$

Dissociation : $\frac{1}{2} \, Cl_{2(g)} \rightarrow Cl_{(g)}$ $\Delta H_2°$

Ionisation : $Na_{(s)} \rightarrow Na^+_{(g)} + e^- \, \Delta H_3°$

E1etron affinity : $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \, \Delta H_4°$

Lattice enthalpy : $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \, \Delta H_5° = ?$

$\Delta H = \Delta H_1° + \Delta H_4° + \Delta H_4° + \Delta H_4° + \Delta H_4°$

$\Delta H = \Delta H_f° - (\Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4°)$

$\Delta H_5° =$ Lattice enthalpy of NaCl.

By the above method, indirectly lattice enthalpy of NaCl is calculated, if the values of $\Delta H_f°$, $\Delta H_1°$, $\Delta H_2°$- $\Delta H_3°$ and $\Delta H_4°$ are given.

52. List the characteristics of Gibbs free energy.

Characteristics of Gibbs free energy:

1. Gibbs free energy is defined as the part of total energy of a system that can be converted (or) available for conversion into work.

$G = H - TS$ ....(1)

Where

H = enthalpy, T = temperature and S = entropy

2. G is a state function and is a single value function.

3. G is an extensive property, whereas ΔG becomes intensive property for a closed system. Both G and ΔG values correspond to the system only.

4. ΔG gives a criteria for spontaneity at constant pressure and temperature.
   - If ΔG is negative ($\Delta G <$ O), the process is spontaneous.
   - If ΔG is positive ($\Delta G >$ O), the process is non-spontaneous.
   - If ΔG is zero ($\Delta G =$ O), the process is equilibrium.

5. For any system at constant pressure and temperature,

$\Delta G = \Delta H - T\Delta S$ .... (2)

We know $AH = \Delta U + P\Delta V$

$\Delta G = \Delta U + P\Delta V - T\Delta S$ ....(3)

6. For the first law of thermodynamics, $\Delta U = q + w$

$\Delta G = q + w + P\Delta V - T\Delta S$ ....(4)

For second law of thermodynamics, $\Delta S = {}_qT$

$\Delta G = q + w + P\Delta V - T_qT$

$\Delta G = w + P\Delta V$ ....(5)

$\Delta G = -w - P\Delta V$ ....(6)

7. $-P\Delta V$ represent the work done due to expansion against a constant external pressure. Therefore, it is clear that the decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion.

8. Unit of Gibb's free energy is J mol^{-1}

53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

Given

n = 2 moles

V_i = 500 ml = 0.5 lit

V_f = 2 lit

T = 25°C = 298 K

$$w = -2.303 \ nRT \ \log \left(\frac{V}{V_i} \right)$$

w = -2.303 x 2 x 8.314 x 298 x log $\frac{2}{0.5}$

w = -2.303 x 2 x 8.314 x 298 x log(4)

w = -2.303 x 2 x 8.314 x 298 x 0.6021

w = -6871 J

w = -6.871 kJ.

54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt ¡n excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1}. Calculate the enthalpy of combustion of the gas in kJ mol^{-1}.

Given,

T_i = 298 K

T_f = 298.45 K

k = 2.5 kJ K

m = 3.5g

M_m = 28

heat evolved = $k\Delta T$

$\Delta H_c = k (T_f - T_i)$

ΔH_c = 2.5 kJ K' (298.45 – 298) K^{-1}

ΔH_c = 1.125 kJ

ΔH_c = 1.1253.5 x 28 kJ mol^{-1}

ΔH_c = 9 kJ mol^{-1}

55. Calculate the entropy change in the system and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C.

Given:

T_{sys} = 77°C = (77 + 273) = 350K

T_{sys} = 33°C = (33 + 273) = 306K

q = 245 J

$$\Delta S_{sys} = \frac{q}{T_{sys}} = \frac{-245}{350} = -0.7 \; JK^{-1}$$

$$\Delta S_{univ} = \frac{q}{T_{sys}} = \frac{+245}{350} = +0.8 \; JK^{-1}$$

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$-245 = —07 3K'

ΔS_{univ} = -0.7 JK^{-1} + 0.8 JK^{-1}

ΔS_{univ} = 0.1 JK^{-1}

56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710 J and expands to 2 litres. Calculate the entropy change in expansion process.

Given,

n = 1 mole

P = 4.1 atm

V = 2Lit

T = ?

q = 3710 J

ΔS = qT

$$\Delta S = \frac{q}{\left(\dfrac{PV}{nR}\right)}$$

$$\Delta S = \frac{nRq}{PV}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

ΔS = 37.10 JK^{-1}

57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 JK^{-1} mol^{-1}. Calculate the melting point of sodium chloride.

Given,

$\Delta H_f(NaCl) = 30.4$ kJ = 30400 J mol^{-1}

$\Delta S_f(NaCl) = 28.4$ JK^{-1} mol^{-1}

$T_f = ?$

$$\Delta S_f = \frac{\Delta H_f}{\Delta T_f}$$

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

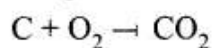$$T_f = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ J K}^{-1}\text{mol}^{-1}}$$

$T_f = 1070.4$ K.

58. Calculate the standard heat of formation of propane, if its heat of combustion is -2220.2 KJ mol^{-1}, the heats of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are – 393.5 and -285.8 kJ mol^{-1} respectively.

Given,
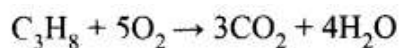
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$\Delta H^0_C = -2220.2$ kJ mol^{-1} ....(1)

$C + O_2 \rightarrow CO_2$

$\Delta H^0_f = -393.5$ kJ mol^{-1} ....(2)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$\Delta H^0_f = -285.8$ kJ mol^{-1} ....(3)

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H^0_C = ?$

$(2) \times 3 \Rightarrow 3C + 3O_2 \rightarrow 3CO_2$

$\Delta H^0_f = -1180.5$ kJ   ....(4)

$(3) \times 4 \Rightarrow 4H_2 + 2O_2 \rightarrow 4H_2O$

$\Delta H^0_f = -1143.2$ kJ   ....(5)

$(4) + (5) - (1)$

$\Rightarrow 3C + 3O_2 + 4H_2 + 2O_2 + 3CO_2 + 4H_2O \rightarrow 3CO_2 + 4H_2O + C_3H_8 + 5O_2$
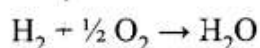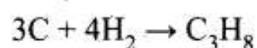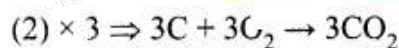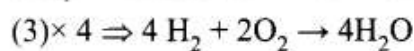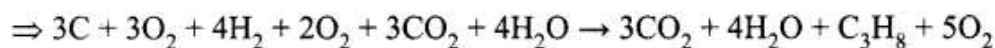
$\Delta H^0_f = -1180.5 - 1143.2 - (-2220.2)$ kJ

$3C + 4H_2 \rightarrow C_3H_8$
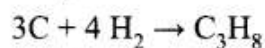
$\Delta H^0_f = -103.5$ kJ mol^{-1}

Standard heat of formation of propane is $\Delta H_f^0(C_3H_8)$ = -103.5 kJ mol^{-1}.

59. You are given normal boiling points and standard enthalpies of vaporization. Calculate the entropy of vaporization of liquids listed below.

S.No.	Liquid	Boiling points (°C)	ΔH (kJ mol^{-1})
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

Answer:

For ethanol:

Given:

T_b = 78.4°C = (78.4 + 273) = 351.4 K

ΔH_v(ethanol) = + 42.4 kJ mol^{-1}

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 42.4 \text{ kJ mol}^{-1}}{351.4 \text{ K}}$$

$$\Delta S_V = \frac{+ 42400 \text{ J mol}^{-1}}{351.4 \text{ K}}$$

ΔH_v = + 91.76 J K^{-1} mol^{-1}

For Toluene:

Given:

T_b = 110.6°C = (110.6 + 273) = 383.6 K

ΔS_v (toluene) = + 35.2 KJ mol^{-1}

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 35.2 \text{ kJ mol}^{-1}}{383.6 \text{ K}}$$

$$\Delta S_V = \frac{+ 35200 \text{ J mol}^{-1}}{383.6 \text{ K}}$$

ΔS_v = + 91.76 J KJ mol^{-1}

60. For the reaction Ag$_2$O$_{(s)}$ → 2Ag$_{(s)}$ + ½ O$_{2(g)}$: ΔH = 30.56 kJ mol^{-1} and ΔS = 6.66 JK^{-1} mol^{-1} (at 1 atm). Calculate the temperature at which AG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

Given,

ΔH = 30.56 kJ mol^{-1}

ΔH = 30560 J mol^{-1}

ΔS = 6.66 x 10^{-3} kJ K^{-1} mol^{-1}

T = ? at which ΔG = 0

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$

$T = \Delta H \Delta S$

$$T = \frac{30.56 \text{ kJ mol}^{-1}}{6.66 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

T = 4589K

(i) At 4589K ; ΔG = 0, the reaction is in equilibrium.

(ii) At temperature below 4598 K, $\Delta H > T \Delta S$

$\Delta G = \Delta H - T\Delta S > 0$, the reaction in the forward direction, is non-spontaneous. In other words the reaction occurs in the backward direction.

61. What is the equilibrium constant K_{eq} for the following reaction at 400K.
$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ given that $AH° = 77.2$ kJ mol^{-1} and $\Delta S° = 122$ JK^{-1} mol^{-1}

Given,

$T = 400$ K ; $\Delta H° = 77.2$ kJ $mol^{-1} = 77200$ J mol^{-1};

$\Delta S° = 122$ JK^{-1} mol^{-1}

$\Delta G° = -2.303$ RT $\log K_{eq}$

$$\log K_{eq} = \frac{\Delta G^0}{2.303 \text{ RT}}$$

$$\log K_{eq} = -\frac{\left(\Delta H^0 - T\Delta S^0\right)}{2.303 \text{ RT}}$$

$$\log K_{eq} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{eq} = -\left(\frac{28400}{7659}\right)$$

$\log K_{eq} = -3.7080$

$K_{eq} = $ anti $\log(-3.7080)$

$K_{eq} = 1.95 \times 10^{-4}$

62. Cyan-amide (NH_2CN) ¡s completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be -742.4 kJ mol^{-1} calculate the enthalpy change of the reaction at 298K.
$NH_2CN_{(s)} + 3/2\ O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$ $\Delta H = ?$

Given,

$T = 298K$; $\Delta U = -742.4$ kJ mol^{-1}

$\Delta H = ?$

$\Delta H = \Delta U + \Delta n_{(g)}RT$

$\Delta H = \Delta U + (n_p - n_r)$ RT

$\Delta H = -742.4 + [2 - 32] \times 8.314 \times 10^{-3} \times 298$

$\Delta H = -742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$

$\Delta H = -742.4 + 1.24$.

$\Delta H = -741.16$ kJ mol^{-1}

63. Calculate the enthalpy of hydrogenation of ethylene from the following data.
Bond energies of C H, C – C, C = C and H – H are 414, 347, 618 and 435 kJ mol^{-1}.
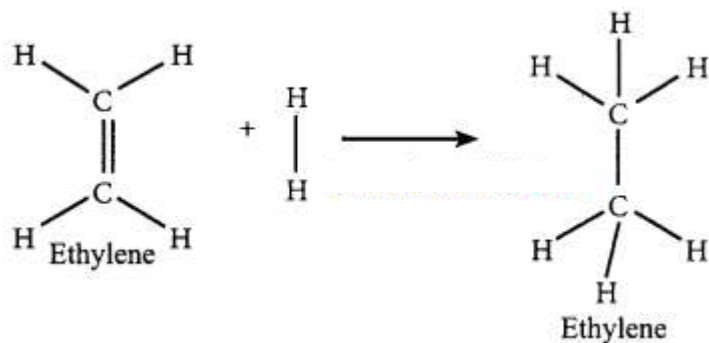
Given,

$E_{C-H} = 414$ kJ mol^{-1}

$E_{C-H} = 347$ kJ mol^{-1}

$E_{C-H} = 618$ kJ mol^{-1}

$E_{H-H} = 435$ kJ mol^{-1}

Ethylene + H₂ → Ethylene (ethane)

$\Delta H_r = \sum(\text{Bond energy})_r - \sum(\text{Bond energy})_P$

$\Delta H_r = (E_{C=C} + 4E_{C-H} + E_{H-H}) - (E_{C-C} + 6E_{C-H})$

$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$
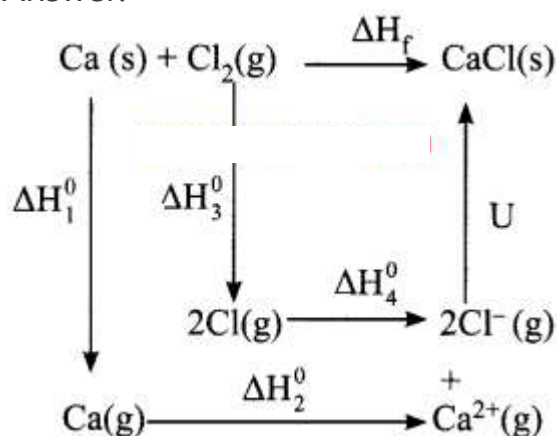
$\Delta H_r = 2709 - 2831$

$\Delta H_r = -122$ KJ mol^{-1}

64. Calculate the lattice enegry of $CaCl_2$ from the given data

$Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)}$ $\Delta H_f^0 = -795$ KJ mol^{-1}

Atomisation : $Ca_{(s)} \rightarrow Ca_{(g)}$ $\Delta H_1° = + 121$ KJ mol^{-1}

Ionization : $Ca_{(g)} \rightarrow Ca^{2+}_{(g)} + 2e^-$ $\Delta H_2° = + 242.8$ KJ mol^{-1}

Dissociation : $Cl_{2(g)} \rightarrow 2 Cl_{(g)}$ $\Delta H_3° = +242.8$ KJ mol^{-1}

Electron affinity : $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ $\Delta H_3° = -355$ KJ mol^{-1}
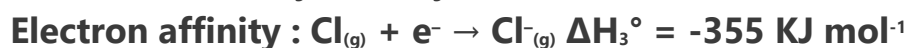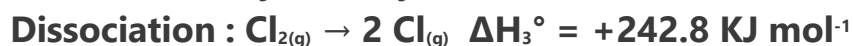
Answer:

$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + 2\Delta H_4 + u$

$-795 = 121 + 2422 + 242.8 + (2 \times -355) + u$

$-795 = 2785.8 - 710 + u$

$-795 = 2075.8 + u$

$u = -795 - 2075.8$

$u = -2870.8$ KJ mol^{-1}

65. Calculate the enthalpy change for the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ from the following data.

$2Fe + \frac{3}{2} O_2 \rightarrow Fe_2O_3;$ $\Delta H = -741$ kJ

$C + \frac{1}{2} O_2 \rightarrow CO;$ $\Delta H = -137$ KJ

$C + O_2 \rightarrow CO_2$ $\Delta H = -394.5$ KJ

Given,

ΔH_f (Fe_2O_3) = -741 kJ mol^{-1}

ΔH_f(CO) = -137 kJ mol^{-1}

ΔH_f(CO_2) = -394.5 kJ mol^{-1}

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ ΔHr = ?

$$\Delta Hr = \sum(\Delta H_f)_{products} - \sum(\Delta H_f)_{reactants}$$

ΔHr = [2 ΔH_f(Fe) + 3 ΔH_f(CO_2)] − [ΔH_f(Fe_2O_3) + 3ΔH_f(CO)]

ΔHr = [- 1183.5] − [-1152]

ΔHr = − 1183.5 + 1152

ΔHr = -31.5 KJ mol^{-1}

66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 13% 1-pentyne(A), 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate AG° for the following equilibria.

B ⇌ A ΔG_1° = ?

B ⇌ C ΔG_2° = ?

T = 175°C = 175 + 273 = 448 K

Concentration of 1 – pentyne [A] = 1.3%

Concentration of 2 – pentyne [B] = 95.2%

Concentration of 1, 2 – pentadiene [C] = 3.5%

At equiLibrium
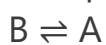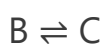
B ⇌ A

95.2% 1.3% ⇒ K$_1$ = 3.595.2 = 0.0 136

B ⇌ C

95.2% 3.5% ⇒ K$_1$ = 1.395.2 = 0.0367

⇒ ΔG_1° = -2.303 RT log K$_1$

ΔG_1° = − 2.303 x 8.3 14 x 448 x log 0.0136

ΔG_1° = + 16010 J

ΔG_1° = + 16 kJ

⇒ ΔG_2°= − 2.303 RT log K$_2$

ΔG_2° = -2.303 x 8.314 x 448 x log 0.0367

ΔG_2° = + 12312 J

ΔG_2° = +12.312 kJ.

67. At 33K. N_2H_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

T = 33K

$N_2O_4 \rightleftharpoons 2NO_2$
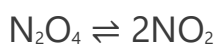
Initial concentration 100%

Concentration dissociated 50%

Concentration remaining at equilibrium 50% – 100%

$K_{eq} = \frac{100}{50} = 2$

$\Delta G° = -2.303$ RT log K_{eq}

$\Delta G° = -2.303$ x 8.31 x 33 x 1og 2
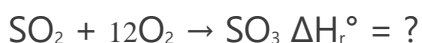
$\Delta G° = -190.18$ J mol^{-1}

68. The standard enthaipies of formation, of SO$_2$ and SO$_3$ are -297, kJ. rnol^{-1} and -396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction:

SO$_2$ + 12 O$_2$ → SO$_3$

Given,

$\Delta G_f°(SO_2) = -297$ KJ mol^{-1}

$\Delta G_f°(SO_2) = -297$ KJ mol^{-1}

$SO_2 + 12O_2 \rightarrow SO_3 \ \Delta H_r° = ?$

$\Delta H_r° = (\Delta H_f°)_{compound} - \sum(\Delta H_f°)_{elements}$

$\Delta H_r° = \Delta H_f° (SO_3) - [\Delta H_f° (SO_2) + 12 \ \Delta H_f° (O_2)]$

$\Delta H_r° = -396$ kJ mol^{-1} $- (-297$ kJ mol^{-1} + 0)

$\Delta H_r° = -396$ kJ mol^{-1} + 297

$\Delta H_r° = -99$ kJmol^{-1}

69. For the reaction at 298 K : 2A + B → C

ΔH = 400 J mol^{-1} ΔS = 0.2 JK^{-1} mol^{-1}

Determine the temperature at which the reaction would be spontaneous.

Given,

T = 298K

$\Delta H = 400$ J mol^{-1}

$\Delta S = 0.2$ J K^{-1} mol^{-1}

$\Delta G = \Delta H - T\Delta S$

if T = 2000K

$\Delta G = 400 - (0.2 \times 2000) = 0$

if T > 2000 K

ΔG will be negative.

The reaction would be spontaneous only beyond 2000 K.

70. Find out the Value of equilibrium constant for the following reaction at 298K, 2 NH$_{3(g)}$ + CO$_{2(g)}$ ⇌ NH$_2$CONH$_{2(aq)}$ + H$_2$O$_{(l)}$

Standard Gibbs energy change, AGr° at the given temperature is – 13.6 kJ mol^{-1}.

Given,

T = 298 K

$\Delta G_r° = -13.6$ kJ mol^{-1}

$= -13600$ J mol^{-1}

$\Delta G° = -2.303$ RT log K_{eq}

$$\log K_{eq} = \frac{-\Delta G°}{2.303RT}$$

$$\log K_{eq} = \frac{13.6 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$\log K_{eq} = 2.38$

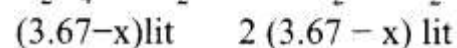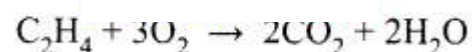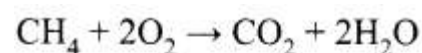K_{eq} = anti log(2.38)

K_{eq} = 239.88.

71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at I atm pressure produce 6.11 lit of carbon dioxide. Find out the amount of heat evolved in kJ, during this combustion. ($\Delta H_c(CH_4)$ = − 890 kJ mol^{-1} and ($\Delta H_c(C2H_4)$= -1423 kJ mol^{-1}.

Given,

ΔH_c (CH_4) = − 890 kJ mol^{-1}

ΔH_c (C_2H_4) = -1423 kJ mol^{-1}

Let the mixture contain x lit of CH_4 and (3.67 − x) lit of ethylene.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
x lit   x lit.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
(3.67−x)lit   2 (3.67 − x) lit

Volume of carbon dioxide formed x + 2 (3.67 − x) 6.11 lit

x + 7.34 − 2x = 6.11

x = 1.23 lit

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$$\Delta H_r^0 = \left[\left(\Delta H_f^0\right)_{products} - \left(\Delta H_f^0\right)_{reactants}\right]$$

$$\Delta H_r^0 = \left[2\left(\Delta H_f^0\right)_{CO_2} + 3\left(\Delta H_f^0\right)_{H_2O}\right] - \left[1\left(\Delta H_f^0\right)_{C_2H_5OH} + 3\left(\Delta H_f^0\right)_{O_2}\right]$$

$$\Delta H_r^0 = \left[\begin{array}{c}2 \text{ mol}(-393.5) \text{ kJ mol}^{-1} \\ +3 \text{ mol}(-285.5) \text{ kJ mol}^{-1}\end{array}\right] - \left[\begin{array}{c}1 \text{ mol}(-277) \text{ kJ mol}^{-1} \\ +3 \text{ mol}(0) \text{ kJ mol}^{-1}\end{array}\right]$$

ΔH_c = [-48.87 kJ mol^{-1}] + [-155 kJ mol^{-1}]

ΔH_c = -203.87 kJ mol^{-1}