(ix) For the redox reaction:

$$Cr_2O_7^{2-} + H^+ + Ni \longrightarrow Cr^{3+} + Ni^{2+} + H_2O$$

the correct coefficients of the reactants for the balanced reaction are:

	$Cr_2O_7^{2-}$	Ni	H ⁺
(A)	1	3	14
(B)	2	3	14
(C)	1	1	16
(D)	3	3	12

ANALYSIS BASED ON MOLE CONCEPT

Section - 2

Let us now solve some numerical problems based on the analysis of redox reactions. In such type of applications based problems, first we have to create a chemical equation and then balance it. And then proceed as per the given problem, using Mole concept.

Illustration - 12 Find the amount of Iron pyrites (FeS₂) which is sufficient to produce enough SO_2 on roasting (heating in excess of O_2) such that it (SO_2) completely decolourises a 1L solution of KMnO₄ containing 15.8 g/L of it.

The equations are :
$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2 and \qquad KMnO_4 + SO_2 \longrightarrow MnSO_4 + H_2SO_4 + K_2SO_4$$

SOLUTION:

First calculate the amount of SO_2 required to decolourise 15.8 g/L of KMnO₄ solution. For this you need to balance the following chemical reaction.

$$\begin{aligned} \text{KMnO}_4 + \text{SO}_2 & & \longrightarrow \\ & \text{MnSO}_4 + \text{H}_2 \text{SO}_4 + \text{K}_2 \text{SO}_4 \end{aligned}$$

Proceeding in the manner as given in above illustrations, we have the balanced equation as:

$$2 \text{ KMnO}_4 + 5 \text{ SO}_2 + 2\text{H}_2\text{O} \longrightarrow$$

$$2 \text{ MnSO}_4 + 2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$$

Now, using our understanding to solve a typical stoichiometric problems, we can solve this problem as follows:

From stoichiometry of balanced equation, we have:

2 moles of
$$KMnO_4 \equiv 5$$
 moles of SO_2

Calculate moles in 15.8 g/L of KMnO₄:

Using: Strength $(g/L) = M M_0$

Molarity =
$$\frac{15.8}{158}$$
 = 0.1 M

$$\Rightarrow$$
 1.0 L of KMnO₄ contains 0.1 moles

Hence moles of
$$SO_2$$
 required = $\frac{5}{2}(0.1) = 0.25$

To calculate the amount of pyrites, we have to balance the reaction:

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

Balancing the reaction (using Hit and Trial Method) we have

$$4 \operatorname{FeS}_2 + 11 \operatorname{O}_2 \longrightarrow 2 \operatorname{Fe}_2 \operatorname{O}_3 + 8 \operatorname{SO}_2$$

From stoichiometry of roasting, we have:

8 moles of
$$SO_2 \equiv 4$$
 moles of FeS_2

0.25 moles of
$$SO_2 = \frac{4}{8}$$
 (0.25) moles of FeS_2
= 0.125 moles of FeS_2

$$\Rightarrow$$
 Mass of FeS₂ = 0.125 × 120 = 15 gm

Illustration - 13 20 mL of a solution containing 0.2 gm of impure sample of H_2O_2 reacts with 0.316 gm of KMn O_4 in presence of H_2SO_4 as per following reaction.

$$\mathrm{KMnO_4} + \mathrm{H_2O_2} + \mathrm{H_2SO_4} \ \longrightarrow \ \mathrm{MnSO_4} + \mathrm{O_2} + \mathrm{H_2O}$$

(a) Find the purity of H_2O_2 solution (b) Calculate the volume of dry oxygen evolved at 27°C and at 760 mm Hg.

SOLUTION:

First write a complete balanced the reaction:

$$2 \text{ KMnO}_4 + 5 \text{ H}_2\text{O}_2 + 3 \text{H}_2\text{SO}_4 \longrightarrow$$

$$2 \text{ MnSO}_4 + \text{K}_2\text{SO}_4 + 5 \text{ O}_2 + 8 \text{ H}_2\text{O}_4$$

From the balanced reaction, we have:

5 moles of $H_2O_2 \equiv 2$ moles of $KMnO_4$

$$Moles of KMnO_4 = \frac{0.316}{158}$$

$$\Rightarrow \qquad \text{Moles of H}_2\text{O}_2 \text{ required} = \frac{5}{2} \times \frac{0.316}{158}$$

$$\Rightarrow$$
 Grams of H₂O₂ = $\frac{5}{2} \times \frac{0.316}{158} \times 34 = 0.17 \text{ gm}$

$$\Rightarrow$$
 % age purity of H₂O₂ = $\frac{0.17}{0.2} \times 100 = 85 \%$

Now: $2 \text{ moles of KMnO}_4 \equiv 5 \text{ moles of O}_2$

Moles of O₂ produced =
$$\frac{5}{2} \times \frac{0.316}{158} = 5 \times 10^{-3}$$

Using PV = nRT we have:

$$V = \frac{nRT}{P} = \frac{5 \times 10^{-3} \times 0.0821 \times 300}{760/760}$$

$$\Rightarrow$$
 V = 0.123 L = 123 mL

Illustration -14 Calculate the amount of SeO_3^{2-} in a solution on the basis of given analysis. 20 mL of M/60 KBr O_3 was added to a sample of SeO_3^{2-} . The bromine evolved was removed and the excess of KBr O_3 was titrated with 5.1 mL of M/25 solution of NaAs O_2 . The reactions involved are: $[A_{Se} = 79 \text{ gm/mol}]$

$$SeO_3^{2-} + BrO_3^- + H^+ \longrightarrow SeO_4^{2-} + Br_2 + H_2O \quad and \quad BrO_3^- + AsO_2^- + H_2O \longrightarrow Br^- + AsO_4^{3-} + H^+ \longrightarrow SeO_4^{3-} + H^+ \longrightarrow SeO_4^{3-}$$

SOLUTION:

In this problem, find the exact amount of $KBrO_3$ used for SeO_3^{2-} (in the first equation) by calculating the excess of $KBrO_3$ with the help of second equation.

Balancing the two equations

(i)
$$5 \text{ SeO}_3^{2-} + 2 \text{BrO}_3^{-} + 2 \text{H}^+ \longrightarrow 5 \text{ SeO}_4^{2-} + \text{Br}_2 + \text{H}_2 \text{O}$$

(ii)
$$BrO_3^- + 3AsO_2^- + 3H_2O \longrightarrow$$

 $Br^- + 3AsO_4^{3-} + 6H^+$

From the equation (ii):

 $3 \text{ m.moles of AsO}_2^- \equiv 1 \text{ m.moles of excess of KBrO}_3$

$$\Rightarrow \frac{1}{25} \times 5.1 \text{ m.moles of AsO}_2^-$$

$$\equiv \frac{1}{3} \times \frac{5.1}{25}$$
 (= 0.068) m.moles of excess of KBrO₃

m.moles of KBrO₂ used in equation (i)

$$=$$
 $\left(\frac{1}{60} \times 20\right) - 0.068 = 0.265$ m.moles

From equation (i):

 $2 \text{ m.moles of KBrO}_3 \equiv 5 \text{ m.moles of SeO}_3^{2-}$

0.265 m.moles of KBrO₃ $\equiv 5/2 (0.265)$ m.moles $\equiv 5/2 (0.265) \times 127$ mg

Mass of
$$SeO_3^{2-} = 84.13 \,\text{mg} = 0.08413 \,\text{g}$$

Illustration - 15 1.0 gms of $AgNO_3$ is dissolved in 50 mL of water. It is titrated with 50 mL of KI solution. The AgI precipitated is filtered off. The excess of KI in the filtrate is titrated with M/10 KIO $_3$ in presence of 6 M HCl till all I^- is converted to ICl. It requires 50 ml of M/10 KIO $_3$ solution. 20 mL of same KI solution requires 30 mL of M/10 KIO $_3$ under same conditions. Determine the percentage of $AgNO_3$ in the sample.

The reaction involved is:

$$KIO_3 + KI + HCl \longrightarrow ICl + KCl + H_2O$$

SOLUTION:

The problem considers three experiments:

- (i) $1.0 \text{ gm AgNO}_3 (50 \text{ mL}) + 50 \text{ mL of KI (M} = ?)$ $AgNO_3 + KI \longrightarrow AgI + KNO_3$
- (ii) Excess of KI + 50 mL of M/10 KIO₃ in 6M HCl KI + KIO₃ + HCl \longrightarrow ICl + KCl + H₂O.
- (iii) To determine the molarity of KI (say M) $20 \text{ mL KI (original)} + 30 \text{ mL of M/}10 \text{ KIO}_3$

First of all you must balance the equation involved in experiments 2 and 3. (Note that the reaction is same in both cases)

$$I^{-} \longrightarrow I^{+} + 2e^{-}$$
 $IO_{3}^{-} + 6 H^{+} + 4e^{-} \longrightarrow I^{+} + 3H_{2}O$

 \Rightarrow The overall balanced equation is:

$$\mathbf{2I^-} + \mathbf{IO_3}^- + \mathbf{6H^+} \longrightarrow \mathbf{3I^+} + \mathbf{3H_2O}$$

 \Rightarrow 2 m.moles of KI = 1 m.moles of KIO₃

Using the above stoichiometry, first find the excess of KI and then molarity of KI

- m.moles of KIO₃ used = $1/10 \times 50 = 5$ 1 m mole of KIO₃ = 2 m. moles of KI
- \Rightarrow 5 m.moles of KIO₃ = 10 m.moles of KI (excess)
 - m.moles of KIO₃ used for titrating 20 mL KI = $1/10 \times 30 = 3$
- \Rightarrow m.moles of KI = 6 = M × 20 \Rightarrow M = 6/20

This gives us initial m.moles of KI in 50 mL volume taken initially.

- Initial m.moles of KI = $(6/20) \times 50 = 15$
- \Rightarrow m.moles of KI used for AgNO₃ = 15 10 = 5

Now, 1 m.mole of KI \equiv 1 m.mole of AgNO₃

- \Rightarrow m.moles of AgNO₃ = 5
- $\Rightarrow \frac{g}{170} \times 1000 = 5 \Rightarrow g = 0.85 \text{ gram}$
- or $\% \text{ AgNO}_3 = 85\% \text{ (mass of sample} = 1 \text{ gm)}$

IMP. Note that n-factor of KBrO₃ in illustration-14 and that of KI in illustration-15 is different in two redox reactions. It is advised to use concept of moles in such cases as done above

IN-CHAPTER EXERCISE - B

- 1. $C_2O_4^{2-}$ can be oxidised to CO_2 by MnO_4^- in acidic as well as in basic medium. What is ratio of moles of MnO_4^- used per mol of $C_2O_4^{2-}$ in acidic medium (Mn^{2+}) to strong basic medium (MnO_4^{2-}) ?
- 2. Calculate number of moles of MnO_4^- required to oxidise 1 mol of $Fe(HC_2O_4)_2$ in acidic medium. How many moles of $Ca(OH)_2$ are required to react with 1 mol of $Fe(HC_2O_4)_2$?
- 3. If $10 \text{ g } V_2O_5$ is dissolved in acid and reduced to V^{2+} by treatment with zinc metal, how many moles of I_2 could be reduced by the resulting V^{2+} solution, as it is oxidised to V^{4+} ? (V=51)

$$V_2O_5 + 10H^+ + 6e^- \longrightarrow 2V^{2+} + 5H_2O$$

- 4. If 94 gm of potassium dichromate react with 3.584 gm of HI, find: $Cr_2O_7^{2-} + HI \longrightarrow CrI_3 + KI + I_2$
 - (i) % age (by mass) of $K_2Cr_2O_7$ left un-reacted (if any),
 - (ii) volume of $I_2(g)$ evolved, if $I_2(s)$ obtained is heated to 546 K and 1.0 atm pressure
- 5. What volume of $0.02\,M\,KMnO_4$ solution is required to oxidise $40.0\,mL$ of $0.1\,M\,FeSO_4$ in presence of H_2SO_4 . Also give the complete balanced chemical reaction.

$$KMnO_4 + FeSO_4 + H_2SO_4 \longrightarrow MnSO_4 + K_2SO_4 + Fe_2(SO_4)_3 + H_2O_4$$

- 6. MnO_4^- can oxidise NO_2^- to NO_3^- in dilute basic medium. How many moles of NO_2^- are oxidised by 1 mol of MnO_4^- ?
- 7. Exactly 40.0 ml of potassium permanganate solution react with 0.8 g of $Na_2C_2O_4$.2 H_2O in the acidic medium according to the reaction: $16H^+(aq) + 2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O$
 - (i) Calculate the normality of permanganate solution. (ii) Calculate the strength of the solution?
- 8. Alcohol levels in the blood can be determined by a redox titration with dichromate solutions in acidic medium according to the balanced equation.

$$C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \longrightarrow 2CO_2(g) + 4Cr^{3+}(aq) + 11H_2O(l)$$

What is the blood alcohol level in mass per cent if $8.76\,\text{mL}$ of $0.05\,\text{M}$ solution is required for titration of a $10.00\,\text{g}$ sample of blood?

- 9. Choose the correct option for each of the following questions. Only one option is correct.
 - (i) $NaIO_3$ reacts with $NaHSO_3$ according to equation: $IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-}$ The weight of $NaHSO_3$ required to react with 100 ml of solution containing 0.66 gm of $NaIO_3$ is:

 (A) 5.2 (B) 4.57 gm (C) 2.3 gm (D) 1.04 gm
 - (ii) $4I^- + Hg^{2+} \longrightarrow HgI_4^{2-}$, 1 mol each of Hg^{2+} and I^- will form $\underline{\hspace{1cm}} HgI_4^{2-}$:
 - (A) 1 mol
- (B) 0.5 mol
- (C) 0.25 mol
- (**D**) 2 mol