

SUBJECTIVE SOLVED EXAMPLES

Example - 1 A polyvalent metal weighing 0.1 gm and having atomic weight of 50 reacted with dilute H_2SO_4 to give 44.8 mL of hydrogen at STP. The solution containing the metal in this Lower oxidation state, was found to require 60 mL of 0.1 N $KMnO_4$ solution for complete oxidation. What are valencies of metal ?

SOLUTION :



$$44.8 \text{ mL } H_2 \text{ at STP} \equiv \frac{44.8}{22400} \text{ moles of } H_2$$

Now, meq of M = meq of H_2

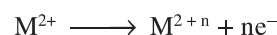
Note : For Hydrogen $2H^+ + 2e^- \longrightarrow H_2$

meq of $H_2 = 2 \times \text{m.moles of } H_2$

$$\Rightarrow \frac{0.1}{50/x} = \left(\frac{44.8}{22400} \right) \times 2 \Rightarrow x = 2$$

Thus, $M \longrightarrow M^{x+} + xe^-$, i.e., oxidation state is +2

Now M^{2+} will acquire higher oxidation state when oxidised by $KMnO_4$



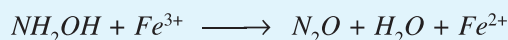
meq of $M^{2+} = \text{meq of } KMnO_4$

$$\frac{0.1}{50/n} \times 1000 = 0.1 \times 60 \Rightarrow n = 3$$

So oxidation state of M is $M^{2+n} \equiv M^{+5}$

Hence the possible valencies are +2, +5.

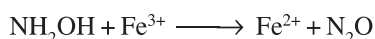
Example - 2 Hydroxylamine (NH_2OH) reduces Fe^{3+} as per following reaction:



Fe^{2+} produced is estimated by titration with $KMnO_4$. A 10 mL sample of NH_2OH is diluted to 1000 mL. 50 mL of this diluted sample is boiled with excess of Fe^{3+} solution. The resulting solution required 12 mL of 0.02M $KMnO_4$ for complete oxidation. Determine the strength of NH_2OH .

SOLUTION :

Consider 50 mL sample :



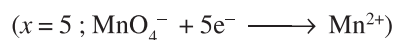
meq of $NH_2OH \equiv \text{meq of } Fe^{3+} \equiv \text{meq of } Fe^{2+}$

Now meq of Fe^{2+} ions are calculated by titrating it against $KMnO_4$.

meq of $Fe^{2+} = \text{meq of } KMnO_4$

Now for calculating meq. of $KMnO_4$, convert molarity (M) into normality (N).

$$N = xM = 5 \times 0.02 = 0.10 \text{ N}$$



meq of Fe^{2+} in 50 mL sample = 0.10×12

$$= 1.2 = \text{meq of } NH_2OH$$

meq of NH_2OH in 1000 mL sample = $1.2 \times 20 = 24$

Now meq. of NH_2OH in original 10 mL = 24

(meq. remain same on dilution)

Now find grams of NH_2OH using $\frac{g}{E} \times 1000 = 24$



Now, $x = \frac{4}{2}$ for 1 mole of NH_2OH

$$\Rightarrow E_{NH_2OH} = \frac{33}{2}$$

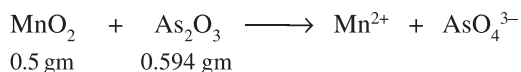
$$\Rightarrow g = \frac{24 \times (33/2)}{1000} = 0.396$$

10 mL sample \equiv 0.396 grams

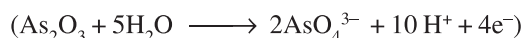
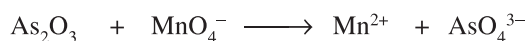
\Rightarrow 1000 mL \equiv 39.6 grams

\Rightarrow Strength of $NH_2OH = 39.6 \text{ g/L}$

Example - 3 A sample of Pyrolusite (MnO_2) weighs 0.5 gm. To this solution 0.594 gm of As_2O_3 and a dil. acid are added. After the reaction has ceased, As^{3+} in As_2O_3 is titrated with 45 mL of $M/50$ $KMnO_4$ solution. Calculate the % age of MnO_2 in pyrolusite.

SOLUTION :

For excess of As_2O_3 :

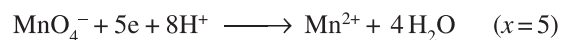


For 1 mole of As_2O_3 , $x = 4$

$$\Rightarrow E_{As_2O_3} = \frac{198}{4}$$

$$\text{meq of } As_2O_3 \text{ taken} = \frac{0.594}{198/4} \times 1000 = 12$$

$$\begin{aligned} \text{meq of excess } As_2O_3 &= \text{meq of } KMnO_4 \\ &= 45 [1/50 \times 5] = 4.5 \end{aligned}$$

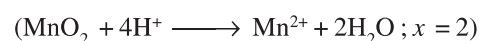


Note that the number of electron transfer for As_2O_3 in two reactions is same.

$$\text{so meq of } As_2O_3 \text{ used for } MnO_2 = 12 - 4.5 = 7.5$$

$$\text{meq of } MnO_2 = 7.5$$

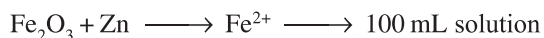
$$\Rightarrow \frac{g}{87/2} \times 1000 = 7.5$$



$$\Rightarrow g = 0.326$$

$$\% MnO_2 = \frac{0.326}{0.5} \times 100 = 65.25\%$$

Example - 4 1 gm of Fe_2O_3 solid of 55.2 % purity is dissolved in acid and reduced by heating the solution with Zn dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution, requires 17 mL of 0.0167 M solution of an oxidant. Calculate the number of electrons taken up by the oxidant in the above reaction.

SOLUTION :

25 mL sample \equiv 17 mL of 0.0167 M of an oxidant.

Let 'n' be the number of electrons taken up by oxidant

Now meq of Fe^{2+} in 25 mL = meq of oxidant

$$= [0.0167 \times n] \times 17 \quad [N = xM]$$

$$\text{meq of } Fe^{2+} \text{ in } 100 \text{ mL} = [0.0167 \times n \times 17] \times 4$$

Also meq of Fe_2O_3 = meq of Fe^{2+} in 100 mL

$$\text{meq of } Fe_2O_3 = \frac{0.552}{E} \times 1000 = (0.0167 \times 68) n$$

$$E_{Fe_2O_3} = ?$$



$$\Rightarrow x = 2 \text{ for 1 mole of } Fe_2O_3$$

$$\Rightarrow E_{Fe_2O_3} = \frac{160}{2} = 80$$

$$\Rightarrow n = \left(\frac{0.552}{80} \times 1000 \right) \div (0.0167 \times 68) = 6$$

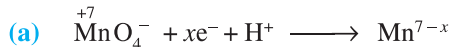
$$\Rightarrow \text{Electrons taken by oxidant} = 6$$

Example - 5 An equal volume of a reducing agent is titrated separately with 1 M $KMnO_4$ in acid, neutral and alkaline media. The volumes of $KMnO_4$ required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reactions. Find out the volume of 1 M $K_2Cr_2O_7$ consumed, if the same volume of the reducing agent is titrated in an acid medium.

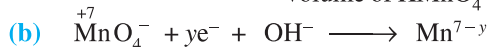
SOLUTION :

Let meq of RA = P (Since equal volume of RA is used in all cases, meq in each case are same.)

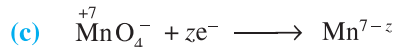
1 M KMnO_4



volume of $\text{KMnO}_4 = 20 \text{ mL}$



volume of $\text{KMnO}_4 = 100 \text{ mL}$



volume of $\text{KMnO}_4 = 33.4 \text{ mL}$

meq of $\text{KMnO}_4 = \text{meq of RA in each case}$

$$(a) P = x \times 1 \times 20 \quad [N = xM]$$

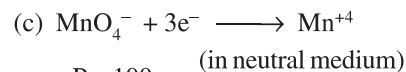
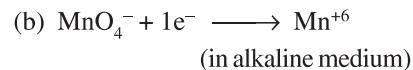
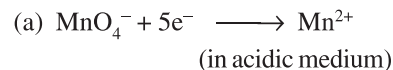
$$(b) P = y \times 1 \times 100$$

$$(c) P = z \times 1 \times 33.4$$

$$\Rightarrow 20x = 100y = 33.4z$$

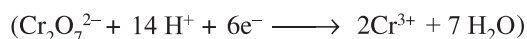
$$\Rightarrow x : y : z \equiv 5 : 1 : 3$$

Balanced half reactions are :



Now this means $P = 100$

meq of RA = meq of $\text{K}_2\text{Cr}_2\text{O}_7$



$$100 = 6 \times 1 \times V$$

$$\Rightarrow V = \frac{100}{6} = 16.67 \text{ mL}$$

Note : Dil. Alkaline KMnO_4 should be considered as Neutral KMnO_4

Example - 6

20 mL of a solution containing oxalic acid and sulphuric acid on titration with 0.05 N NaOH required 40 mL of the base. 20 mL of same solution on titration with 0.02 N KMnO_4 required 50 mL of KMnO_4 . Determine the strength of oxalic acid and H_2SO_4 .

SOLUTION :

In this problem, two type of titrations viz : Neutralisation and Redox are involved. Note that in both cases, the volume of sample is same, i.e., mmoles of two constituents are same in both.

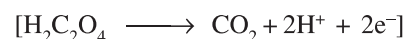
Let $x = \text{mmoles of H}_2\text{C}_2\text{O}_4$ and $y = \text{mmoles of H}_2\text{SO}_4$
In first titration, both $\text{H}_2\text{C}_2\text{O}_4$ and H_2SO_4 react with base (as acids). [n-factor of both being 2 due to 2H^+ per mole in each].

$$\Rightarrow 2 \times x + 2 \times y = \text{meq of NaOH} = 40 \times 0.05 = 2$$

$$\Rightarrow x + y = 1$$

In second titration, only $\text{H}_2\text{C}_2\text{O}_4$ (being reducing agent) reacts with KMnO_4 .

$$\Rightarrow 2 \times x = \text{meq of KMnO}_4 = 50 \times 0.02 = 1$$



Note : In the above reaction H_2SO_4 also reacts with KMnO_4 but in the same reaction with $\text{H}_2\text{C}_2\text{O}_4$ so the meq. of H_2SO_4 should not be added separately. $[\text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Mn}^{2+} + \text{CO}_2]$

Hence $x = y = 0.5 \text{ mmoles}$

$$\Rightarrow \frac{g_{\text{H}_2\text{C}_2\text{O}_4}}{M_{\text{H}_2\text{C}_2\text{O}_4}} \times 1000 = 0.5 \Rightarrow g = 0.045 \text{ gm}$$

$$\text{Strength of H}_2\text{C}_2\text{O}_4 = \frac{0.045}{20/1000} = 2.25 \text{ g/L}$$

$$\text{Similarly, } \frac{g_{\text{H}_2\text{SO}_4}}{M_{\text{H}_2\text{SO}_4}} \times 1000 = 0.5 \Rightarrow g = 0.049 \text{ gm}$$

$$\text{Strength of H}_2\text{SO}_4 = \frac{0.049}{20/1000} = 2.45 \text{ g/L}$$

Example - 7 The neutralisation of a solution of 1.2 gm of mixture of $H_2C_2O_4 \cdot 2H_2O$ and $KHC_2O_4 \cdot H_2O$ and some impurities which are neutral, consumed 40.0 mL of 0.25 N NaOH. On the other hand, on titration with $KMnO_4$ in acidic medium, 0.4 gm of mixture required 40.0 mL of 0.125 N $KMnO_4$. Find the molar ratio of the components.

SOLUTION :

Note that the mass of two samples is different in two titrations.

Let $x =$ mmoles of $H_2C_2O_4 \cdot 2H_2O$

and $y =$ mmoles of $KHC_2O_4 \cdot H_2O$ in 0.4 g sample

So mmoles of oxalic acid in 1.2 gm sample $= 3x$

and mmoles of bioxalate in 1.2 gm sample $= 3y$

1. Neutralisation with NaOH :

meq of $H_2C_2O_4 \cdot 2H_2O$ + meq of $KHC_2O_4 \cdot H_2O$
 $=$ meq of NaOH

$$2 \times 3x + 1 \times 3y = 0.25 \times 40$$

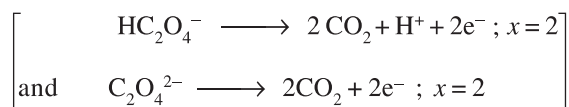
[oxalic acid has 2 H^+ ions while bioxalate has only 1 H^+]

$$\Rightarrow 2x + y = \frac{10}{3} \quad \dots \text{(i)}$$

2. Redox reaction with $KMnO_4$:

meq of $H_2C_2O_4 \cdot 2H_2O$ + meq of $KHC_2O_4 \cdot H_2O$
 $=$ meq of $KMnO_4$

$$2 \times x + 2 \times y = 0.125 \times 40$$



$$\Rightarrow x + y = 2.5 \quad \dots \text{(ii)}$$

Solve for x and y to get : $x = \frac{5}{6}$ and $y = \frac{5}{3}$

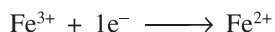
$$\Rightarrow x : y = 1 : 2$$

Example - 8 A sample of $Fe_2(SO_4)_3$ and FeC_2O_4 was dissolved in H_2SO_4 . 40 mL of $N/16$ $KMnO_4$ were required for complete oxidation. After oxidation, the mixture was reduced by Zn/H_2SO_4 . On again oxidation by same $KMnO_4$, 60 mL of it were required. Calculate the ratio of millimoles of $Fe_2(SO_4)_3$ and FeC_2O_4 .

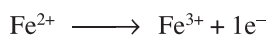
SOLUTION :

Let m.moles of $Fe_2(SO_4)_3 = x$

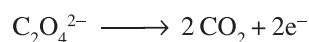
and m.moles of $FeC_2O_4 = y$



x mmol $Fe_2(SO_4)_3 \equiv 2x$ mmol $Fe^{3+} \equiv 2x$ meq Fe^{3+}



y mmol $FeC_2O_4 \equiv y$ mmol $Fe^{2+} \equiv y$ meq Fe^{2+}



y mmol $C_2O_4^{2-} \equiv 2y$ meq $C_2O_4^{2-}$

In the first titration

meq of $KMnO_4 =$ meq of $Fe^{2+} +$ meq of $C_2O_4^{2-}$

$$1/16 \times 40 = y + 2y \text{ (Fe}^{3+} \text{ will not be oxidised further)}$$

$$\Rightarrow y = 40/48$$

Zn reduces whole of Fe^{3+} (Fe^{3+} : original and Fe^{3+} from FeC_2O_4) to Fe^{2+}

In the second titration

So total meq of $Fe^{2+} = 2x + y$

meq of $KMnO_4 =$ meq of Fe^{2+}

$$1/16 \times 60 = (2x + y)$$

$$\Rightarrow 2x + y = \frac{60}{16} \Rightarrow x = \frac{70}{48}$$

Ratio of millimoles $= x : y = 7 : 4$

Example - 9 A 4:3 molar mixture of Cu_2S and CuS was titrated with 200 mL of 0.75 M KMnO_4 in acidic medium producing SO_2 , Cu^{2+} . The SO_2 was boiled off and the excess of MnO_4^- was titrated with 175 mL of 1 M Fe^{2+} solution. Find the moles of CuS and Cu_2S in the original mixture.

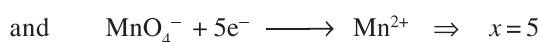
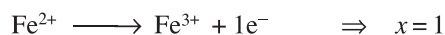
SOLUTION :

Note that in Cu_2S , both Cu_2^+ and S^{2-} will get oxidize

Let x = mmoles of Cu_2S ; y = mmoles of CuS

$$\Rightarrow \frac{x}{y} = \frac{4}{3} \Rightarrow 3x = 4y \quad \dots\dots (i)$$

Now, First find excess of KMnO_4



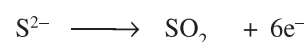
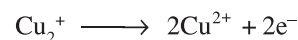
$$\text{meq of Fe}^{2+} = (1 \times 1) \times 175 = 175$$

$$\Rightarrow \text{excess meq. of KMnO}_4 = 175$$

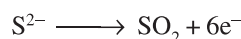
$$\text{Now, meq of KMnO}_4 \text{ taken} = 200 \times (0.75 \times 5) = 750$$

$$\Rightarrow \text{meq of KMnO}_4 \text{ used for Cu}_2\text{S and CuS} \\ = 750 - 175 = 575 \text{ meq.}$$

$$\Rightarrow \text{meq of Cu}_2\text{S} + \text{meq of CuS} = 575 \dots\dots (ii)$$

Oxidation of Cu_2S 

$$1 \text{ mole of Cu}_2\text{S} \equiv 8e^- \Rightarrow n - \text{factor} = 8$$

Oxidation of CuS 

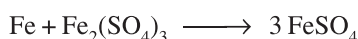
$$1 \text{ mole of CuS} \equiv 6e^- \Rightarrow n - \text{factor} = 6$$

$$\text{Using (ii), } x \times 8 + y \times 6 = 575$$

$$\Rightarrow \left(\frac{4}{3} \cdot y\right) \times 8 + y \times 6 = 575 \text{ [Using (i)]}$$

$$\Rightarrow x = 46 \text{ mmoles and } y = 34.5 \text{ mmoles}$$

Example - 10 25 mL of a solution of ferric alum $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ containing 2.41 gm of salt was boiled with iron when the reaction $\text{Fe} + \text{Fe}_2(\text{SO}_4)_3 \longrightarrow 3\text{FeSO}_4$ takes place. The un-reacted iron was filtered off and the solution was treated with 0.1 N KMnO_4 in acidic medium. What is the titre value (vol. of KMnO_4) of KMnO_4 ? If Cu had been used in place of iron, what would have been titre value?

SOLUTION :

$$1 \text{ mole of Fe}_2(\text{SO}_4)_3 \equiv 3 \text{ moles of FeSO}_4$$

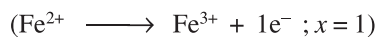
$$1 \text{ mole of Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O} \\ \equiv 1 \text{ mole of Fe}_2(\text{SO}_4)_3$$

$$\frac{2.41}{964} \text{ moles of salt} \equiv \frac{2.41}{964} \text{ mole of Fe}_2(\text{SO}_4)_3$$

$$\equiv \frac{3 \times 2.41}{964} \text{ moles of FeSO}_4$$

Now, meq of $\text{FeSO}_4 \equiv$ meq of KMnO_4 .

$$\left(\frac{3 \times 2.41}{964}\right) \times 1000 = 0.1 \times V$$



$$\Rightarrow V = 75 \text{ mL}$$

$$\therefore \text{Titre value} = 75 \text{ mL}$$

If Cu were used in place of Fe

$$1 \text{ mole} \qquad \qquad \qquad 2 \text{ mole}$$

(only FeSO_4 reacts with KMnO_4)

$$\frac{2.41}{964} \text{ mol Fe}_2(\text{SO}_4)_3 \equiv 2 \times \frac{2.41}{964} \text{ mol FeSO}_4$$

$$\text{meq of FeSO}_4 \equiv \text{meq of KMnO}_4$$

$$\Rightarrow \left(\frac{2 \times 2.41}{964}\right) \times 1 \times 1000 = 0.1 \times V$$

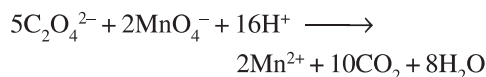
$$\Rightarrow V = 50 \text{ mL}$$

$$\therefore \text{Titre value} = 50 \text{ mL}$$

Example - 11 A solution of 0.2 gm of a compound containing cupric and oxalate ions on titration with 0.02 M potassium permanganate in presence of sulphuric acid consumes 22.6 mL of the oxidant. The resultant solution is neutralised with sodium carbonate, acidified with dil. acetic acid and treated with excess of KI. The iodine liberated required 11.3 mL of 0.05 M sodium thiosulphate solution for complete reduction. Find the mole ratio of two ions. Also write down the balanced redox reactions involved in the above titrations.

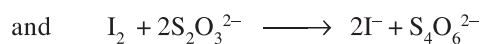
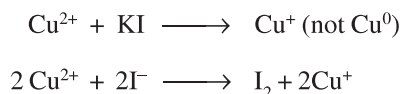
SOLUTION :

Cu^{2+} ion can not be oxidised, so only $\text{C}_2\text{O}_4^{2-}$ will be oxidised by KMnO_4 .



2 millimoles of $\text{MnO}_4^- \equiv 5$ millimoles of $\text{C}_2\text{O}_4^{2-}$ ions

0.02×22.6 m.moles of $\text{MnO}_4^- \equiv 5/2 (0.02 \times 22.6)$ m.moles
= 1.13 m.moles of oxalate ions

Important :

2 millimoles of $\text{S}_2\text{O}_3^{2-} \equiv 1$ millimoles of I_2

(0.05×11.3) mmol $\text{S}_2\text{O}_3^{2-} \equiv 1/2 (0.05 \times 11.3)$ mmol I_2
= 0.2825 mmol I_2

Also, 1 mmol $\text{I}_2 \equiv 2$ mmol Cu^{2+}

0.2825 m.mol $\text{I}_2 \equiv 2 \times 0.2825$ mmol Cu^{2+}
= 0.565 mmol Cu^{2+}

So, mole ratio of $\frac{\text{C}_2\text{O}_4^{2-}}{\text{Cu}^{2+}} = \frac{1.13}{0.565} = 2$

Example - 12 25 ml solution containing 6.35 g/L of $\text{K H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ required V_1 ml of 0.1 N NaOH and V_2 ml of 0.1 N KMnO_4 in two separate titrations. Calculate V_1 and V_2 .

SOLUTION :

$\text{K H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O} : M_0 = 254 \text{ gm / mol}$

(a) meq of compound (as acid) \equiv meq of NaOH

$$25 \times N_a = V_1 \times 0.1$$

\Rightarrow where $N_a = \frac{S}{E} = \frac{6.35}{254/3} = 0.075$

[Note : 3 acidic Hydrogens]

$\Rightarrow V_1 = \frac{25 \times 0.075}{0.1} = 18.75 \text{ ml}$

(b) meq of compound (as RA) = meq of KMnO_4

$$25 \times N_{\text{RA}} = V_2 \times 0.1$$

where $N_{\text{RA}} = \frac{S}{E} = \frac{6.35}{254/4} = 0.10$

$\Rightarrow V_2 = \frac{25 \times 0.1}{0.1} = 25 \text{ ml}$

[Note : n - factor = 4 due to 2 moles of $\text{C}_2\text{O}_4^{2-}$]

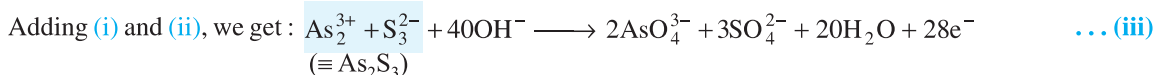
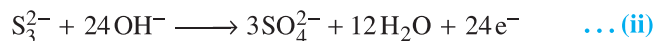
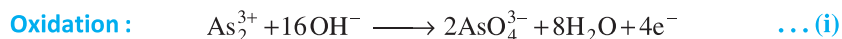
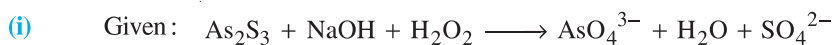
Example - 13 Three solutions, each of 100 ml containing 0.3M As_2S_3 , 4.5M NaOH and 4.5M H_2O_2 respectively were mixed to form AsO_4^{3-} and SO_4^{2-} as products.

(i) Give a balanced redox equation.

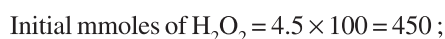
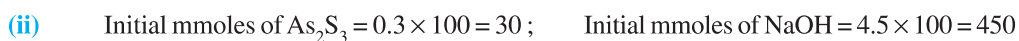
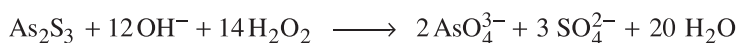
(ii) Calculate the molarity of each species left at the end of the reaction.

(iii) If the above solution is allowed to stand for sometime, what volume of O_2 will be collected at STP ?

SOLUTION :



Multiply (iii) by 1 and (iv) by 14 and add to get :



It is clear from the balanced equation and mmoles of reactants that As_2S_3 is the limiting reagent.

