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 :

$$\text{Metal (M)} + H_2SO_4 \longrightarrow H_2$$

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

Now, meq of M = meq of H_2

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

meq of $H_2 = 2 \times$ m.moles of H_2

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

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

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

$$M^{2+} \longrightarrow M^{2+n} + ne^-$$

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

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

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:*

$$NH_2OH + Fe^{3+} \longrightarrow N_2O + H_2O + Fe^{2+}$$

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* 0.02*M* $KMnO_4$ *for complete oxidation. Determine the strength of* NH_2OH*.*

SOLUTION :

Consider 50 mL sample :

$$NH_2OH + Fe^{3+} \longrightarrow Fe^{2+} + N_2O$$

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

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

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

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

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

$$(x = 5 \; ; \; MnO_4^- + 5e^- \longrightarrow Mn^{2+})$$

meq of Fe^{2+} in 50 mL sample $= 0.10 \times 12$

$= 1.2 =$ 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 $\frac{g}{E} \times 1000 = 24$

$$2\,NH_2OH \longrightarrow N_2O + H_2O + 4H^+ + 4e^-$$

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

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

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

10 mL sample ≡ 0.396 grams

$\Rightarrow$ 1000 mL ≡ 39.6 grams

$\Rightarrow$ Strength of NH_2OH = 39.6 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 :

$$\underset{0.5\text{ gm}}{MnO_2} + \underset{0.594\text{ gm}}{As_2O_3} \longrightarrow Mn^{2+} + AsO_4^{3-}$$

For excess of As_2O_3 :

$$As_2O_3 + MnO_4^- \longrightarrow Mn^{2+} + AsO_4^{3-}$$

$$E_{As_2O_3} = ? \qquad \mathbf{As_2O_3 \longrightarrow AsO_4^{3-}}$$

$$(As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-)$$

For 1 mole of As_2O_3, $x = 4$

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

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

$$\text{meq of excess } As_2O_3 = \text{meq of } KMnO_4$$

$$= 45\,[1/50 \times 5\,] = 4.5$$

$$MnO_4^- + 5e + 8H^+ \longrightarrow Mn^{2+} + 4H_2O \qquad (x = 5)$$

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

so meq of As_2O_3 used for MnO_2 $= 12 - 4.5 = 7.5$

meq of $MnO_2 = 7.5$

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

$$(MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O\,;\ x = 2)$$

$$\Rightarrow \quad g = 0.326$$

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

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 :

$$Fe_2O_3 + Zn \longrightarrow Fe^{2+} \longrightarrow 100\text{ mL solution}$$

25 mL sample ≡ 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

$$= [\,0.0167 \times n] \times 17 \qquad [N = xM]$$

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

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

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

$$E_{Fe_2O_3} = ?$$

1 mole of $Fe_2O_3 \equiv 2Fe^{3+}$; $Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$

$\Rightarrow$ $x = 2$ for 1 mole of Fe_2O_3

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

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

$\Rightarrow$ 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 $KMnO_4$

(a) $\overset{+7}{Mn}O_4^- + xe^- + H^+ \longrightarrow Mn^{7-x}$

volume of $KMnO_4 = 20$ mL

(b) $\overset{+7}{Mn}O_4^- + ye^- + OH^- \longrightarrow Mn^{7-y}$

volume of $KMnO_4 = 100$ mL

(c) $\overset{+7}{Mn}O_4^- + ze^- \longrightarrow Mn^{7-z}$

volume of $KMnO_4 = 33.4$ mL

meq of $KMnO_4$ = meq of RA in each case

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

(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 :

(a) $MnO_4^- + 5e^- \longrightarrow Mn^{2+}$ (in acidic medium)

(b) $MnO_4^- + 1e^- \longrightarrow Mn^{+6}$ (in alkaline medium)

(c) $MnO_4^- + 3e^- \longrightarrow Mn^{+4}$ (in neutral medium)

Now this means P = 100

meq of RA = meq of $K_2Cr_2O_7$

$(Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O)$

$100 = 6 \times 1 \times V$

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

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 = mmoles of $H_2C_2O_4$ and y = mmoles of H_2SO_4
In first titration, both $H_2C_2O_4$ 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 $H_2C_2O_4$ (*being reducing agent*) reacts with $KMnO_4$.

$\Rightarrow$ $2 \times x = \text{meq of } KMnO_4 = 50 \times 0.02 = 1$

$[H_2C_2O_4 \longrightarrow CO_2 + 2H^+ + 2e^-]$

Note : In the above reaction H_2SO_4 also reacts with $KMnO_4$ but in the same reaction with $H_2C_2O_4$ so the meq. of H_2SO_4 should not be added separately. $[H_2C_2O_4 + KMnO_4 + H_2SO_4 \longrightarrow Mn^{2+} + CO_2]$

Hence $x = y = 0.5$ mmoles

$$\Rightarrow \quad \frac{g_{H_2C_2O_4}}{M_{H_2C_2O_4}} \times 1000 = 0.5 \quad \Rightarrow g = 0.045 \text{ gm}$$

$$\text{Strength of } H_2C_2O_4 = \frac{0.045}{20/1000} = 2.25\text{ g / L}$$

$$\text{Similarly, } \frac{g_{H_2SO_4}}{M_{H_2SO_4}} \times 1000 = 0.5 \quad \Rightarrow g = 0.049 \text{ gm}$$

$$\text{Strength of } H_2SO_4 = \frac{0.049}{20/1000} = 2.45\text{ g / L}$$

Example - 7 *The neutralisation of a solution of 1.2 gm of mixture of $H_2C_2O_4.2H_2O$ and $KHC_2O_4.H_2O$ 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 $H_2C_2O_4 . 2H_2O$

and $y =$ mmoles of $KHC_2O_4 . H_2O$ 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 $H_2C_2O_4 . 2H_2O$ + meq of $KHC_2O_4 . H_2O$

= 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^+]

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

2. Redox reaction with $KMnO_4$:

meq of $H_2C_2O_4.2H_2O$ + meq of $KHC_2O_4 . H_2O$

= meq of $KMnO_4$

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

$$\left[\begin{array}{lll} & HC_2O_4^- \longrightarrow 2\,CO_2 + H^+ + 2e^- \; ; \; x = 2 \\ \text{and} & C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \; ; \; x = 2 \end{array}\right]$$

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

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

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

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 $FeC_2O_4 = y$

$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$

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

$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$

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

$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2e^-$

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 $C_2O_4^{2-}$

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

$\Rightarrow \quad y = 40/48$

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+}

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

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

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

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

Now, First find excess of $KMnO_4$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \quad \Rightarrow \quad x = 1$$

and $MnO_4^- + 5e^- \longrightarrow Mn^{2+} \Rightarrow x = 5$

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

$\Rightarrow$ excess meq. of $KMnO_4 = 175$

Now, meq of $KMnO_4$ taken $= 200 \times (0.75 \times 5) = 750$

$\Rightarrow$ meq of $KMnO_4$ used for Cu_2S and CuS

$= 750 - 175 = 575$ meq.

$\Rightarrow$ meq of Cu_2S + meq of CuS = 575 ......(ii)

Oxidation of Cu_2S

$$Cu_2^+ \longrightarrow 2Cu^{2+} + 2e^-$$

$$S^{2-} \longrightarrow SO_2 + 6e^-$$

1 mole of $Cu_2S \equiv 8e^- \Rightarrow$ n – factor = 8

Oxidation of CuS

$$S^{2-} \longrightarrow SO_2 + 6e^-$$

1 mole of CuS $\equiv 6e^- \Rightarrow$ n – factor = 6

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

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

$\Rightarrow x = 46$ mmoles and $y = 34.5$ mmoles

Example - 10 *25 mL of a solution of ferric alum $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ containing 2.41 gm of salt was boiled with iron when the reaction $Fe + Fe_2(SO_4)_3 \longrightarrow 3Fe(SO_4)$ 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 :

$$Fe + Fe_2(SO_4)_3 \longrightarrow 3\,FeSO_4$$

1 mole of $Fe_2(SO_4)_3 \equiv 3$ moles of $FeSO_4$

1 mole of $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\,H_2O$

$\equiv 1$ mole of $Fe_2(SO_4)_3$

$\frac{2.41}{964}$ moles of salt $\equiv \frac{2.41}{964}$ mole of $Fe_2(SO_4)_3$

$\equiv \frac{3 \times 2.41}{964}$ moles of $FeSO_4$.

Now, meq of $FeSO_4 \equiv$ meq of $KMnO_4$.

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

$(Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \; ; x = 1)$

$\Rightarrow V = 75$ mL

$\therefore$ Titre value = 75 mL

If Cu were used in place of Fe

$$Cu + Fe_2(SO_4)_3 \longrightarrow 2\,FeSO_4 + CuSO_4$$

1 mole 2 mole

(only $FeSO_4$ reacts with $KMnO_4$)

$\frac{2.41}{964}$ mol $Fe_2(SO_4)_3 \equiv 2 \times \frac{2.41}{964}$ mol $FeSO_4$

meq of $FeSO_4 \equiv$ meq of $KMnO_4$

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

$\Rightarrow V = 50$ mL

$\therefore$ Titre value = 50 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 $C_2O_4^{2-}$ will be oxidised by $KMnO_4$.

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

2 millimoles of $MnO_4^- \equiv$ 5 millimoles of $C_2O_4^{2-}$ ions

0.02×22.6 m.moles of $MnO_4^- \equiv 5/2\,(0.02 \times 22.6)$ m.moles $= 1.13$ m.moles of oxalate ions

Important :

$$Cu^{2+} + KI \longrightarrow Cu^+ \text{ (not } Cu^0\text{)}$$

$$2\,Cu^{2+} + 2I^- \longrightarrow I_2 + 2Cu^+$$

and $\quad I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

2 millimoles of $S_2O_3^{2-} \equiv$ 1 millimoes of I_2

(0.05×11.3) mmol $S_2O_3^{2-} \equiv 1/2\,(0.05 \times 11.3)$ mmol I_2

$= 0.2825$ mmol I_2

Also, $\quad$ 1 mmol $I_2 \equiv$ 2 mmol Cu^{2+}

0.2825 m.mol $I_2 \equiv 2 \times 0.2825$ mmol Cu^{2+}

$= 0.565$ mmol Cu^{2+}

So, mole ratio of $\dfrac{C_2O_4^{2-}}{Cu^{2+}} = \dfrac{1.13}{0.565} = 2$

Example - 12 *25 ml solution containing 6.35 g/L of K $H_3(C_2O_4)_2 .2H_2O$ 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 :

$K\,H_3(C_2O_4)_2 . 2H_2O \;:\; M_0 = 254$ gm / mol

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

$25 \times N_a = V_1 \times 0.1$

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

[Note : 3 acidic Hydrogens]

$\Rightarrow \quad V_1 = \dfrac{25 \times 0.075}{0.1} = 18.75$ ml

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

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

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

$\Rightarrow \quad V_2 = \dfrac{25 \times 0.1}{0.1} = 25$ml

[Note : n – factor = 4 due to 2 moles of $C_2O_4^{2-}$]

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 :

(i) Given : $As_2S_3 + NaOH + H_2O_2 \longrightarrow AsO_4{}^{3-} + H_2O + SO_4{}^{2-}$

Oxidation : $As_2^{3+} + 16\,OH^- \longrightarrow 2AsO_4^{3-} + 8H_2O + 4e^-$ . . . (i)

$S_3^{2-} + 24\,OH^- \longrightarrow 3SO_4^{2-} + 12\,H_2O + 24\,e^-$ . . . (ii)

Adding (i) and (ii), we get : $\underset{(\equiv As_2S_3)}{As_2^{3+} + S_3^{2-}} + 40OH^- \longrightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O + 28e^-$ . . . (iii)

Reduction : $H_2O_2 + 2e^- \longrightarrow 2OH^-$ . . . (iv)

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

$$As_2S_3 + 12\,OH^- + 14\,H_2O_2 \longrightarrow 2\,AsO_4^{3-} + 3\,SO_4^{2-} + 20\,H_2O$$

(ii) Initial mmoles of $As_2S_3 = 0.3 \times 100 = 30$; Initial mmoles of $NaOH = 4.5 \times 100 = 450$

Initial mmoles of $H_2O_2 = 4.5 \times 100 = 450$;

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

mmoles of NaOH left $= 450 - 12 \times 30 = 90$ $\Rightarrow$ $M_{NaOH} = \dfrac{90}{300} = 0.3\,M$

mmoles of H_2O_2 left $= 450 - 14 \times 30 = 30$ $\Rightarrow$ $M_{H_2O_2} = \dfrac{30}{300} = 0.1\,M$

mmoles of AsO_4^{3-} formed $= 2 \times 30 = 60$ $\Rightarrow$ $M_{AsO_4^{3-}} = \dfrac{60}{300} = 0.2\,M$

mmoles of SO_4^{2-} formed $= 3 \times 30 = 90$ $\Rightarrow$ $M_{SO_4^{2-}} = \dfrac{90}{300} = 0.3\,M$

mmoles of H_2O formed $= 20 \times 30 = 600$ $\Rightarrow$ $M_{H_2O} = \dfrac{600}{300} = 2\,M$

(iii) If a H_2O_2 solution is allowed to stand, it decomposes to give O_2 and H_2O.

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}\,O_2$$

Thus, mmoles of O_2 formed $= 30 \times \dfrac{1}{2} = 15$

or, volume of O_2 at STP $= 15 \times 22.4 \times 10^{-3}\,L = 0.336\,L$ [$\because$ 1 mole of O_2 at STP $\equiv 22.4\,L$]