

CONCEPT OF GRAM EQUIVALENTS

Section - 3

In the method of gram-equivalents (milli-equivalents), there is no need to balance a redox reaction. For example, let us consider a *typical redox reaction* (consisting of two reactants and two main products):



According to concept of gram equivalent (or meq) ;

$$1 \text{ gm.eq. of X} \equiv 1 \text{ gm.eq. of Y} \equiv 1 \text{ gm eq. of A} \equiv 1 \text{ gm eq. of B}$$

or meq. of an oxidising agent = meq. of a reducing agent

Note : $\text{gm.eq.} = \frac{g}{E}$ and $\text{meq} = \frac{g}{E} \times 1000$

Now to understand the method of gram-equivalents more clearly, let us understand the following illustrations very carefully.

Illustrating the concept :

What volume of a deci-normal solution of $K_2Cr_2O_7$ is required to oxidise 1.0 gm of Tin (Sn) in presence of HCl to its highest oxidation state ?

The involved reaction is :



Here, Sn is a reducing agent (RA) and $K_2Cr_2O_7$ is an oxidant (OA).

So applying the concept of gram-equivalent, we have :

$$\text{gm.eq of OA (} K_2Cr_2O_7 \text{)} = \text{gm.eq of RA (Sn)}$$

Using the definition : $N V_L = \frac{g}{E}$, we get :

$$\begin{aligned} \frac{1}{10} \times V_L &= \frac{1}{E_{Sn}} ; \quad E_{Sn} = \frac{119}{x} \quad \text{where } x = \text{electron transfer / mol (also known as valence or n-factor)} \\ Sn &\longrightarrow Sn^{4+} + 4e^- \Rightarrow x = 4 \\ \Rightarrow \frac{V}{10} &= \frac{1}{119/4} \Rightarrow V = \frac{40}{119} = 0.336L = 336 \text{ mL} \end{aligned}$$

Note : From definition of gram-equivalents $\left(\text{gm.eq.} = \frac{g}{E} = N V_L \right)$, it is very clear that, we must be very confident about the concept of equivalent weight (E), for an oxidising or reducing agent. So first let us learn intricacies of the concept of equivalent weight for an oxidant(s) and reductant(s) in detail.

Equivalent Weight (E) of Oxidant and Reductant :

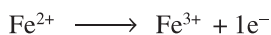
The equivalent weight of an oxidising or reducing agent is defined as :

$$\text{Equivalent weight} = E = \frac{M_0}{x}$$

where M_0 = molecular mass ; x = number of electrons transferred (loss or gain) by **one mole of oxidising or reducing agent** as given by their balanced ionic half reaction.

Illustrating the concept :**➤ FeSO_4 (Ferrous Sulphate)**

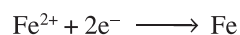
As reducing agent :



1 mole of e's are transferred /mole of FeSO_4 ,
so $x = 1$

$$\Rightarrow E_{\text{FeSO}_4} = \frac{M_0}{x} = \frac{152}{1} = 152$$

As an oxidising agent :



$$\Rightarrow x = 2$$

$$\Rightarrow E_{\text{FeSO}_4} = \frac{M_0}{x} = \frac{152}{2}$$

Note : FeSO_4 (ferrous sulphate) acts both as an oxidant and as a reductant

➤ $\text{H}_2\text{C}_2\text{O}_4$ (Oxalic acid) or $\text{C}_2\text{O}_4^{2-}$ (Oxalate ion)

As reducing agent

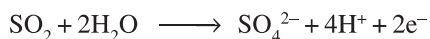


$$x = 2 \text{ or } E_{\text{H}_2\text{C}_2\text{O}_4} = \frac{90}{2}$$

Note : $E_{\text{Na}_2\text{C}_2\text{O}_4} = \frac{134}{2}$; $E_{\text{CaC}_2\text{O}_4} = \frac{128}{2}$ as n-factor for $\text{C}_2\text{O}_4^{2-}$ is always 2
Sodium oxalate Calcium oxalate

➤ SO_2 (Sulphur Dioxide)

As reducing agent



$$x = 2 \Rightarrow E_{\text{SO}_2} = \frac{64}{2}$$

➤ HI (Hydrogen Iodide)

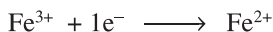
As reducing agent only



$$x = \frac{2}{2} = 1 \text{ (for 1 mole of HI)} \Rightarrow E_{\text{HI}} = \frac{128}{1}$$

➤ **Fe₂(SO₄)₃** (Ferric sulphate)

As oxidising agent only



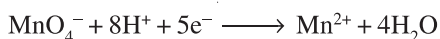
Since 1 mole of Fe₂(SO₄)₃ ≡ 2 moles of Fe³⁺

$$\Rightarrow x = 2 \text{ for 1 mole of Fe}_2(\text{SO}_4)_3$$

$$\Rightarrow E_{\text{Fe}_2(\text{SO}_4)_3} = \frac{400}{2}$$

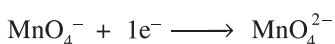
➤ **KMnO₄** (Potassium Permanganate)

As oxidising agent in acidic medium



$$x = 5 \Rightarrow E_{\text{KMnO}_4/\text{H}^+} = \frac{158}{5}$$

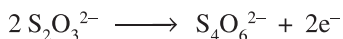
As oxidising agent in strong alkaline medium



$$x = 1 \Rightarrow E_{\text{KMnO}_4} = \frac{158}{1}$$

➤ **Na₂S₂O₃** (Sodium Thiosulphate)

As reducing agent in acidic medium

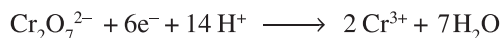


$$x = 2/2 = 1 \text{ for 1 mole of Na}_2\text{S}_2\text{O}_3$$

$$\Rightarrow E_{\text{Na}_2\text{S}_2\text{O}_3/\text{H}^+} = \frac{158}{1}$$

➤ **K₂Cr₂O₇** (Potassium Dichromate)

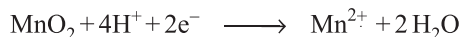
As oxidising agent only



$$x = 6 \Rightarrow E_{\text{K}_2\text{Cr}_2\text{O}_7} = \frac{294}{6}$$

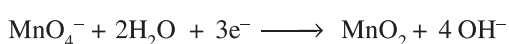
➤ **MnO₂** (Manganese dioxide)

As oxidising agent in acidic medium



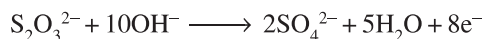
$$x = 2 \Rightarrow E_{\text{MnO}_2} = \frac{87}{2}$$

As oxidising agent in dilute alkaline medium



$$x = 3 \Rightarrow E_{\text{KMnO}_4/\text{OH}^-} = \frac{158}{3}$$

As reducing agent in alkaline medium



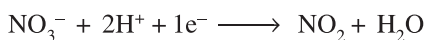
$$x = 8$$

$$\Rightarrow E_{\text{Na}_2\text{S}_2\text{O}_3/\text{OH}^-} = \frac{158}{8}$$

Note: From the above case, you should observe carefully that the equivalent weight depends upon medium.

➤ **HNO₃** (Nitric Acid)

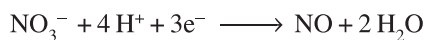
As oxidising agent (conc. HNO₃)



$$x = 1$$

$$\Rightarrow E_{\text{HNO}_3(\text{conc.})} = \frac{63}{1} = 63$$

As oxidising agent (dil. HNO₃)



$$x = 3$$

$$\Rightarrow E_{\text{HNO}_3(\text{dil})} = \frac{63}{3} = 21$$

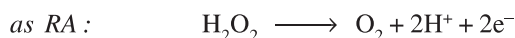
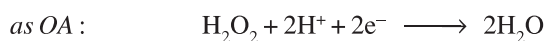
Note: Equivalent weight depends on dilution for HNO₃.

Try to Calculate 'E'

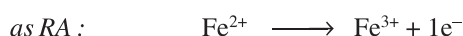
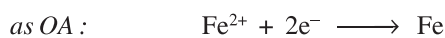


Note: Some substances act both as OA (oxidants) and reductants (RA) in different reactions. Like FeSO_4 , H_2O_2 , HNO_2 etc

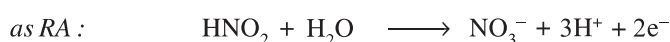
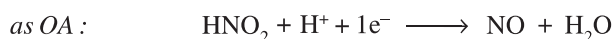
H_2O_2 (Hydrogen Peroxide)



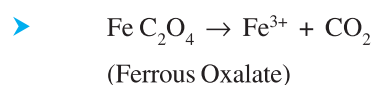
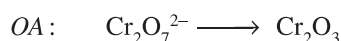
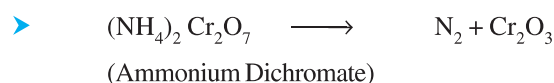
FeSO_4 (Ferrous Sulphate)



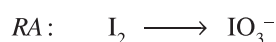
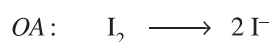
HNO_2 (Nitrous Acid)



Some other type of oxidants and reductants are also given below.



Note: In FeC_2O_4 both cations and anions are oxidised.



(same compound as OA/RA)

Note: Some compounds act as Acids and RA or OA in separate experiments.

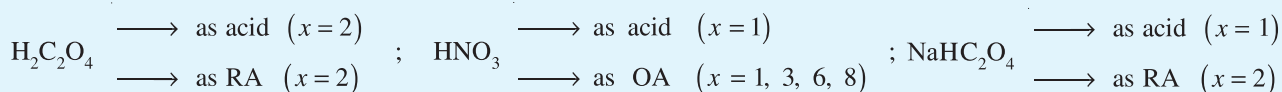
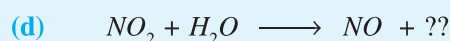
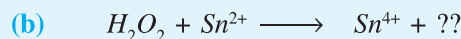
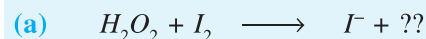


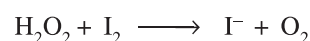
Illustration - 16 Complete and balance the following.



SOLUTION :

- (a) I_2 is reduced to I^- , so H_2O_2 must be oxidised, i.e., it acts as a reducing agent. Hence final product will be O_2 gas.

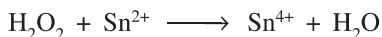
The complete chemical equation is :



The balanced equation will be :



- (b) $\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+}$, i.e., Sn^{2+} is oxidised. So H_2O_2 acts as an oxidising agent, which means it must be reduced to H_2O .

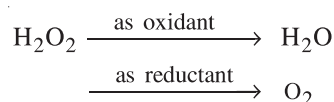


The balanced equation will be :

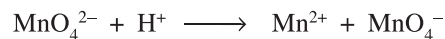


Important Note :

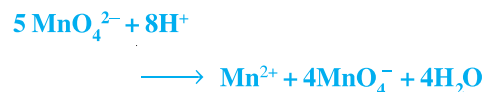
H_2O_2 is chemical species acting both as a reducing agent and as an oxidising agent.



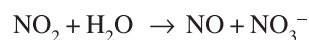
- (c) MnO_4^{2-} is reduced to Mn^{2+} , i.e it is acting as an oxidising agent. Now H^+ is already in the maximum oxidation state, so MnO_4^{2-} must also be reduced to Mn^{7+} state i.e. MnO_4^- will be formed. Hence it is a case of disproportionation reaction.



The balanced equation will be :



- (d) NO_2 (+4 state) disproportionate (like in last case) to NO (+2 state) and NO_3^- (+5 state).



The balanced equation will be :



Equivalent weight of a compound undergoing disproportionation :

Let a compound 'A' contains an ion 'X' undergoing disproportionation.

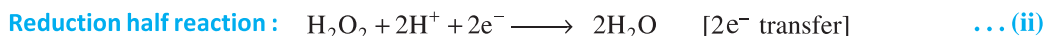
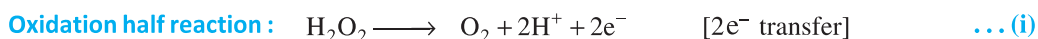
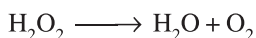
$$\text{Then, } E_A = \text{Equivalent weight of A} = \frac{\text{Effective molecular weight of A}}{\text{Number of } e^- \text{ transfer}}$$

$$\text{where Effective molecular weight of A} = \left(\frac{\text{Total weight of A in}}{\text{Oxidation half reaction}} \right) + \left(\frac{\text{Total weight of A in}}{\text{Reduction half reaction}} \right)$$

1. When number of e^- transfer are same in oxidation and reduction half reactions

Illustrating the concept :

H_2O_2 undergoes disproportionation in acidic medium given by the following reaction :

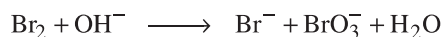


Thus, Effective molecular mass of $\text{H}_2\text{O}_2 = \underset{\text{from (i)}}{M_{\text{H}_2\text{O}_2}} + \underset{\text{from (ii)}}{M_{\text{H}_2\text{O}_2}} = 2M_{\text{H}_2\text{O}_2}$

$$\Rightarrow E_{\text{H}_2\text{O}_2} = \frac{2M_{\text{H}_2\text{O}_2}}{2} = 34$$

2. When number of e^- transfer are different in oxidation and reduction half reactions**Illustrating the concept :**

Br_2 undergoes disproportionation in basic medium given by the following reaction:



Now, Effective molecular mass of $Br_2 = \underset{\text{from (i)}}{M_{Br_2}} + \underset{\text{from (ii)}}{5M_{Br_2}} = 6M_{Br_2}$

Note : $5M_{Br_2}$ is taken because we have to equalize the number of electrons in both oxidation and reduction.

Thus, $E_{Br_2} = \frac{6M_{Br_2}}{10} = 0.6 M_{Br_2} = 96$

This means n-factor of Br_2 is $\frac{10}{6}$

Note : However, we should use "Mole concept" while solving problems based on such reactions.

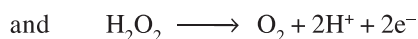
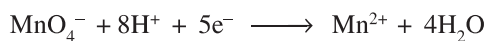
Illustration - 17 1.0 gram of a sample of H_2O_2 solution containing y% H_2O_2 by weight requires y mL of $KMnO_4$ solution for complete titration under acidic condition. Find the molarity of $KMnO_4$ solution.

SOLUTION :

This question involves a redox reaction between H_2O_2 (RA) and $KMnO_4$ (OA). Let us apply the concept of gram (milli) equivalents to solve this problem.

i.e., $\text{meq of } H_2O_2 = \text{meq of } KMnO_4$

Let us find n-factor (valence factor) of H_2O_2 and $KMnO_4$ as follows.



$x = 5$ for $KMnO_4$ and $x = 2$ for H_2O_2

$$\text{meq of } H_2O_2 = \frac{1 \times \left(\frac{y}{100}\right)}{E_{H_2O_2}} \times 1000 \left[E_{H_2O_2} = \frac{34}{2} \right]$$

$$\text{meq of } KMnO_4 = N(y)$$

$$\Rightarrow \frac{1 \times \left(\frac{y}{100}\right)}{17} \times 1000 = N(y) \Rightarrow N = \frac{10}{17}$$

$$\text{And Molarity} = \frac{N}{x}; x = 5 \text{ for } KMnO_4/H^+$$

$$\Rightarrow M = \frac{10/17}{5} = \frac{2}{17} = 0.117$$

Illustration - 18 A solution of $KMnO_4/H^+$ containing 3 gm/L is used to titrate H_2O_2 solution containing 2 gm/L. What volume of $KMnO_4$ will be required to react with 20 mL of H_2O_2 solution? Also find the strength of H_2O_2 in terms of available oxygen.

SOLUTION :

This redox reaction is a typical one.

$$N_{\text{KMnO}_4} = \frac{\text{strength}}{E} = \frac{3}{158/5} = \frac{15}{158}$$

$$N_{\text{H}_2\text{O}_2} = \frac{\text{strength}}{E} = \frac{2}{17}$$

Now using equation of titration

meq. of OA = meq of RA

$$\Rightarrow N_{\text{OA}} V_{\text{OA}} = N_{\text{RA}} V_{\text{RA}} \quad (\text{meq} = NV_{\text{cc}})$$

$$\frac{15}{158} \times V = \frac{2}{17} \times 30$$

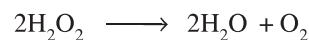
$$\Rightarrow V = 24.8 \text{ mL}$$

What is strength in terms of available oxygen ?

It is also called as volume strength of H_2O_2 .

Try yourself : Express the volume strength of H_2O_2 sample if 100 cc of H_2O_2 solution were diluted with 100 cc of water. 10 cc of this diluted solution required 20 cc of M/50 KMnO_4 in presence of H_2SO_4 for complete titration. [Ans : 2.24 vol H_2O_2]

Volume strength is the volume of O_2 given out at S.T.P. by 1 volume solution of H_2O_2 .



$$2 \text{ mol } \text{H}_2\text{O}_2 \equiv 1 \text{ mol of } \text{O}_2 \equiv 22.4 \text{ L of } \text{O}_2$$

$$1 \text{ mol } \text{H}_2\text{O}_2 \equiv 1/2 \text{ mol of } \text{O}_2 \equiv 11.2 \text{ L of } \text{O}_2 \text{ per 1.0 L}$$

$$\Rightarrow \mathbf{1 \text{ M } \text{H}_2\text{O}_2 \equiv 11.2 \text{ vol of } \text{O}_2 \text{ at STP}}$$

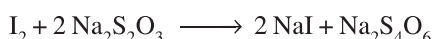
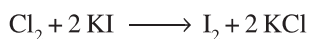
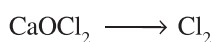
$$\text{or } \mathbf{1 \text{ N } \text{H}_2\text{O}_2 \equiv 5.6 \text{ vol of } \text{O}_2}$$

In the present question :

$$\frac{2}{17} N \text{H}_2\text{O}_2 \equiv \frac{2}{17} \times 5.6 = 0.66 \text{ L of } \text{O}_2$$

It is written as : 0.66 vol H_2O_2

Illustration - 19 1.25 gm of a sample of bleaching powder (CaOCl_2) is dissolved in 100 mL of water. 25 mL of it are treated with KI solution. The iodine so liberated required 12.5 mL of M/25 hypo solution ($\text{Na}_2\text{S}_2\text{O}_3 / \text{H}^+$) for complete titration. Find the percentage of available chlorine from the sample of bleaching powder.

SOLUTION :

In 25 ml sample :

meq of Cl_2 in bleaching powder

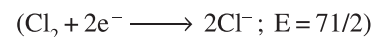
= meq of I_2 liberated = meq of hypo solution

$$\text{meq of Hypo} = NV_{\text{cc}} = \left(1 \times \frac{1}{25}\right) \times 12.5 = 0.5$$

$$\Rightarrow \text{meq of } \text{Cl}_2 / 25\text{ml.} = 0.5$$

$$\Rightarrow \text{meq of } \text{Cl}_2 \text{ in } 100 \text{ mL} = (0.5 \times 4)$$

$$\Rightarrow \frac{g}{E} \times 1000 = 2$$



$$g = \frac{2}{1000} \times \frac{71}{2} = 0.071 \text{ gms}$$

% available chlorine

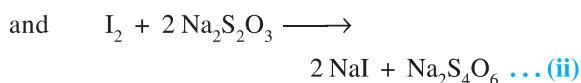
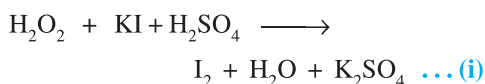
$$= \frac{g \text{ Cl}_2}{g \text{ CaOCl}_2} \times 100 = \frac{0.071}{1.25} \times 100 = 5.68 \%$$

Try yourself : 5.0 gm of CaOCl_2 is dissolved in water to make 500 mL solution. 20 mL of it is acidified with acetic acid and treated with KI solution. The iodine liberated required 20 mL of M/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution. Find the percentage of available chlorine. [Ans: 35.5%]

Illustration - 20 50 ml of an aqueous solution of H_2O_2 was titrated with an excess of KI solution in dilute H_2SO_4 , the liberated iodine required 20 ml of 0.1 N $Na_2S_2O_3$ solution for complete reaction. Calculate volume strength of H_2O_2 solution.

SOLUTION :

Both the chemical equations involved in the problems are typical redox reactions.



Now : meq. of I_2 = meq. of $Na_2S_2O_3$ (in eq (ii))

$$\Rightarrow \text{meq. of } I_2 = 20 \times 0.1 = 2$$

and meq. of H_2O_2 = meq. of I_2 (in eq (i))

$$N_{H_2O_2} \times V_{H_2O_2} = 2$$

$$\Rightarrow N_{H_2O_2} = \frac{2}{50} = \frac{1}{25}$$

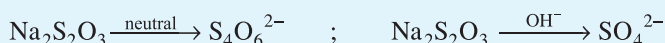
Now, 1 N H_2O_2 solution = 5.6 vol. of O_2

$$\Rightarrow \frac{1}{25} N \text{ } H_2O_2 \text{ solution} = 5.6 \times \frac{1}{25}$$

$$= 0.224 \text{ vol of } O_2$$

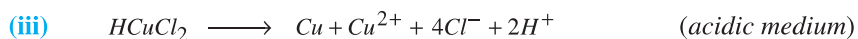
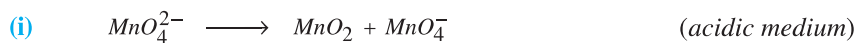
\Rightarrow Volume Strength of H_2O_2 solution = 0.224 vol.

Note : In above two problems, $Na_2S_2O_3$ is used as reducing agent (very common and important reductant). You must remember its action in neutral and basic both, though neutral medium (hypo solution) is more important.

**IN-CHAPTER EXERCISE - C**

1. An excess of acidified solution of potassium iodide was added to 20 millilitres of hydrogen peroxide solution and the iodine so liberated required 15 ml of 0.4 N sodium thiosulphate solution for iodometric titration. Calculate the volume strength of H_2O_2 solution.
2. 0.4 g sample of a copper ore was converted into copper sulphate solution. The resulting solution was acidified with dilute acetic acid and excess KI added. The liberated iodine required 0.248 g $Na_2S_2O_3 \cdot 5H_2O$ for complete reaction. What is the percentage of copper in the ore ?
3. 0.367 g of a mixture containing sodium oxalate and potassium oxalate requires 125 ml of 0.04 N $KMnO_4$ for titration at the end -point. What is the percentage of sodium oxalate in the mixture ?
4. 0.1 M $KMnO_4$ is used for the titrating hypo solution. What volume of the solution in ml will be required to react with 0.158g of $Na_2S_2O_3$?
5. 5.5 g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ requires 5.4 ml of 0.1 N $KMnO_4$ solution for complete oxidation. Calculate the gram mole of hydrated ferric sulphate in the mixture.
6. Find equivalent weight of $Fe(HC_2O_4)_2$ as : (a) an Acid (b) a reducing agent.
7. 3.55 gm of bleaching powder are ground to a fine paste with water and made up to 100 mL. 25 mL of this after addition of KI and dilute acetic acid required 20 mL of 0.125 N thiosulphate solution. Calculate the percentage of available chlorine in the sample of bleaching powder.

8. Calculate equivalent weight of underlined species in the following unbalanced reactions:



9. Choose the correct option for each of the following questions. Only one option is correct.

(i) 10 ml of a solution of H_2O_2 labelled '10 volume' just decolorizes 100 ml of KMnO_4 solution acidified with dilute H_2SO_4 . Calculate the amount of KMnO_4 in the given solution.

- (A) 0.1563 gm (B) 0.563 gm (C) 5.63 gm (D) 0.256 gm

(ii) The equivalent mass of $\text{Na}_2\text{S}_2\text{O}_3$ in the reaction with I_2 is equal to :

- (A) $\frac{\text{molar mass}}{2}$ (B) $\frac{\text{molar mass}}{3}$ (C) $\frac{\text{molar mass}}{4}$ (D) molar mass

(iii) In basic medium CrO_4^{2-} reacts with $\text{S}_2\text{O}_3^{2-}$ resulting in formation of $\text{Cr}(\text{OH})_4^-$ and SO_4^{2-} . How many ml of 0.1 M Na_2CrO_4 are required to react with 40 ml of 0.25 M $\text{Na}_2\text{S}_2\text{O}_3$?

- (A) 240.2 mL (B) 24.02 mL (C) 266.67 mL (D) 26.67 mL

(iv) KI reacts with H_2SO_4 producing I_2 and H_2S . The volume of 0.2 M H_2SO_4 required to produce 3.4 gm of H_2S is :

- (A) 4L (B) 2.5L (C) 3.8L (D) 5L

(v) A 0.46 gm sample of As_2O_3 required 25.0 ml of KMnO_4 solution for its titration. The molarity of KMnO_4 solution is :

- (A) 0.016 (B) 0.074 (C) 0.032 (D) 0.128

(vi) Number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ reduced by 1 mole of Sn^{+2} is :

- (A) 1/3 (B) 1/6 (C) 2/3 (D) 1

(vii) 10 ml of H_2O_2 solution (volume strength = x) required 10 ml of N/0.56 MnO_4^- solution in acidic medium. Hence x is :

- (A) 0.56 (B) 5.6 (C) 0.1 (D) 10

(viii) Equivalent weight of H_3PO_2 (mol. wt. = M) when it disproportionates into PH_3 and H_3PO_3 is :

- (A) M (B) M/2 (C) M/4 (D) 3M/4