

## Chapter Three :

### Quantitative volumetric analysis :

**Titration** : one of the quantitative volumetric analysis , it used to determine the analyte by find the volume of standard reagent (solution) required to completely react with it ( ) .

$aA + bB \rightarrow \text{products}$                       where : A = titrant (st. sol.)

B = titrate (analyte)

a,b = no. of moles

**Note** : Explain the conditions of titration (for students) .

**Equivalent point** : The point in which the amount of standard sol. Is chemically equivalent to the substance that is to be determined.

**End point** : is based upon the physical changes that occur in a solution in titration method . the end point detection including change in color , electrical potential , current and conductivity.

Best titration , when that the volume difference between end point and equivalent point is small. (when the end point is exactly same the equivalent point) .

**Primary standard** : a highly purified substance that required as a reference material in titration , and the accuracy of volumetric analysis is dependent on it .

Primary standard should be includes :

- a) Highest purity.                      b) Stability.
- c) Absence of hydrate water.      d) High equivalent weight.

**Standard solution** : Is the solution whose its concentration is known exactly.

There are two ways for prepare standard solution :

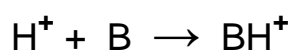
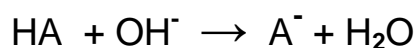
- 1) Directly , by dissolving a carefully weight quantity of pure reagent and diluting to an exactly known volume .
- 2) Indirectly , by titrating a weighed quantity of pure substance with the reagent solution .

Standard solution should be :

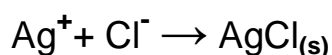
- a) Remain stable for months .
- b) Rapid and completely react with analyte .
- c) Observed satisfactory end point .
- d) Balanced chemical equation .

### **Types of titration reactions :**

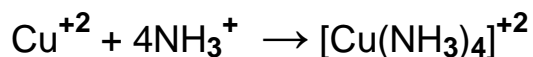
1) Acid-base titration(neutralization titration):



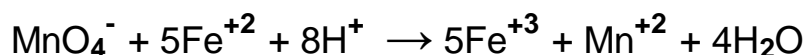
2) Precipitation titration :



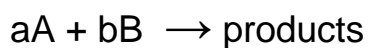
3) Complex formation :



4) Oxidation-reduction reaction :



### **Calculation associated with titrimetric methods :**



(analyte)

where : A = titrant (st. sol.)

B = titrate

$$R = \frac{b}{a} =$$

$$\frac{\text{m.mole of analyte}}{\text{m.mole of titrant}}$$

1) no. of m.moles of A :

$$M = \frac{\text{m.moles}}{\text{ml}} = \frac{\text{mole}}{\text{L}}$$

$$\text{m.mole A} = M_A \cdot V_A$$

2) no. of m.moles of B :

$$\text{m.moles of B} = M_A \cdot V_A \cdot R$$

3) weight of B :

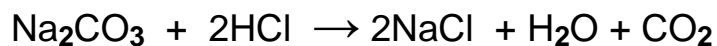
$$\text{m.moles B} = \frac{\text{mg (B)}}{\text{M.wt.(B)}}$$

$$\text{mg of B} = M_A \cdot V_A \cdot R \cdot \text{M.wt. B}$$

4) percentage of B :

$$\% \text{ B} = \frac{\text{mg (B)}}{\text{mg of sample}} \times 100$$

**EX.** Calculate the percentage of  $\text{Na}_2\text{CO}_3$  in 1gm of sample dissolved in water and titrated with standard sol. of 0.1M HCl , volume of HCl required is 36.5ml ?



$$R = \frac{b}{a} = 1$$

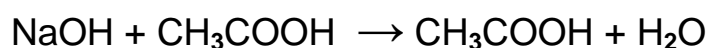
$$\% \text{Na}_2\text{CO}_3 = \frac{\text{mg}(\text{Na}_2\text{CO}_3)}{\text{mg of sample}}$$

$$\text{mg of Na}_2\text{CO}_3 = M_{\text{HCl}} \cdot V_{\text{HCl}} \cdot R \cdot \text{M.wt. Na}_2\text{CO}_3 \cdot R$$

$$\text{mg of Na}_2\text{CO}_3 = 0.1 \times 36.5 \times 106 \times 0.5 = 193.45 \text{ mg}$$

$$\% \text{Na}_2\text{CO}_3 = \frac{193.45 \text{ mg}}{1000 \text{ mg}} \times 100 = 19.345 \%$$

**EX.** Calculate weight of acetic acid found in 5ml of vinegar titrated with 0.1M of NaOH , vol. required = 35ml , M.wt. acetic acid = 60 ?



$$R = \frac{b}{a} = 1$$

$$\text{mg CH}_3\text{COOH} = M_{\text{NaOH}} \cdot V_{\text{NaOH}} \cdot R \cdot \text{M.wt. CH}_3\text{COOH} \cdot R$$

$$\text{mg CH}_3\text{COOH} = 0.1 \times 35 \times 60 \times 1 = 210 \text{ mg}$$

### Dilution calculations :

$$M_1V_1 = M_2V_2$$

$$N_1V_1 = N_2V_2$$

**EX.** Prepare 250ml of 0.05N HCl , from a sol. of 0.1N ?

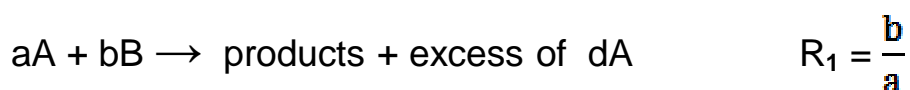
$$N_1V_1 = N_2V_2$$

$$0.1 \times V_1 = 0.05 \times 250$$

$$V_1 = 125 \text{ ml}$$

### Back- titration :

In this type of titration , when the reaction is slow and the end point is not clear and when we need to determine analyte like B , it is convenient or necessary to added an excess amount from A , and the excess amount will be determine by back-titration with a second (another) standard sol. like C .



$$\text{mg B} = [N_A V_A - N_C V_C] \times \text{eq.wt. B} \times R_1$$

**EX.** 10ml of 0.05M EDTA was added to a sol. contain zirconium ion  $Zr^{+4}$ , the excess of EDTA was titrated with a sol. of 0.05M of bismuth nitrate  $BiNO_3$ , and the vol. was 208ml. calculate weight of Zr in sol. ,

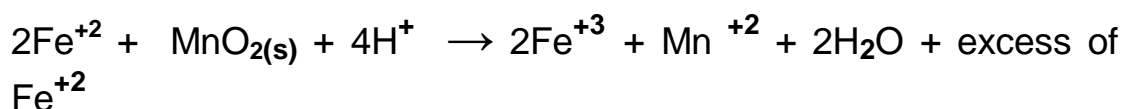
$$A.wt\ Zr = 91\ ?$$



$$mg\ of\ Zr = [(10 \times 0.05) - (2.8 \times 0.054)] \times 91 \times (R_1=1)$$

$$mg\ of\ Zr = 35.9\ mg$$

**EX.** 50ml of 0.1N  $FeSO_4$  is added to a sol. of  $MnO_2$ , then the excess from  $FeSO_4$  was titrated with a sol. of 0.08N  $K_2Cr_2O_7$ . calculate percentage of  $MnO_2$ ? wt.of sample = 200mg, M.wt.  $MnO_2 = 87$ , vol.of tit. = 16ml.



$$eq.wt.\ MnO_2 = \frac{87}{2} = 43.5$$

$$mg\ FeSO_4 = 50 \times 0.1 = 5\ mg$$

$$mg\ of\ excess\ FeSO_4 = 16 \times 0.08 = 1.28\ mg$$

$$mg\ of\ FeSO_4\ equivalent\ to\ MnO_2 = 5 - 1.28 = 3.72\ mg$$

$$\% MnO_2 = \frac{3.72 \times 43.5 \times (R=1)}{200\ mg} \times 100 = 80.8\%$$