Chapter Four

Methods of preparation solutions and chemical calculations in volumetric titration reactions

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| 4 | **Methods of preparation solutions and chemical calculations in volumetric titration reactions.** |

4.1 Standard and Standardised Solutions .

A Standard solution is the solution of accurately known concentration, such as 0.1 N Na_2CO_3, 0.1 N Borax (0.1 N $Na_2B_4O_7.10H_2O$), 0.1M $H_2C_2O_4$ and 0.1 N or 0.1 M NaCl solutions.

These standard solutions are prepared from the primary standard materials by direct weighing.

A Standardised solution is a solution of approximate concentration which can be known exactly by standardisation it with standard solution, Such as preparation of approximately 0.1 M or 0.1 N HCl and standardise it with a standard solution of Na_2CO_3 or Borax. Standard solutions of Na_2CO_3 and Borax can be prepared from the pure solid materials by weighing.

When the standardised solution is prepared and standardised, its properties become identical to the properties of the standard solution.

4.2 Characteristics of standard solution:

1- Its concentration remains constant for months or years, or at least within the period of titration.

2- It rapidly reacts with the analyte and the reaction is complete within the period of the experiment.

3- Its reaction with the analyte can be expressed as balanced equation in order to get the exact weight of the analyte.

4- A sudden change of the reaction should occur in order to identify the equivalence point of the reaction by suitable chemical indicator.

Examples: solutions of oxalic acid (0.1 N), sodium carbonate (0.1 N), sodium chloride (0.1 N) and borax (0.1 N).

4.3 Primary standard materials.

It is a material or chemical of high purity and characterised by the following requirements:

1- Its purity should not be less than 99.5%, otherwise a purification method should be available to confirm its purity.

2- It should be stable and not be hydrated or efflorescent.

3- It can be easily obtained and not expensive.

4- It is preferred to have high equivalent weight. For example, if we compare the equivalent weights of Na_2CO_3 (53) and borax (191), we find that the equivalent wt. of borax is four times larger than sodium carbonate. If we want to prepare 0.1 N of both solutions we should use: 1.325 g Na_2CO_3 and 4.775 g borax.

If an error of 0.02 g is occurred in weighing, therefore the percentages of error equal:

$$\frac{0.02}{1.325} \times 100 = 1.6\% \quad \text{and} \quad \frac{0.02}{4.775} \times 100 = 0.4\% \quad \text{respectively.}$$

Therefore, the percentage of error with Na_2CO_3 is four times higher than borax. As the weight is increased, the percentage of error is decreased.

5- The primary standard material is easily soluble in water or the applicable solvent. Examples: oxalic acid, sodium carbonate, borax, sodium chloride and zinc sulphate hepta hydrate.

4.4 Methods of preparation of solutions.

4.4.1 From solid materials.

The solid material may be/primary standard material, therefore, the prepared solution is standard. If the solid material is not primary standard, the prepared solution is not standard (has an approximate concentration).

Ex(1): Show, by calculation, how could you prepare 250 ml of 0.1 N Na_2CO_3 from the solid primary standard of Na_2CO_3.

The solution:

Eq. wt. on $Na_2CO_3 = \dfrac{2\times23 + 12 + 3\times16}{2} = \dfrac{106}{2} = 53$ g/mol

Number of equivalents of solid Na_2CO_3 = Number of equivalents of Na_2CO_3 in solution.

Also:

Number of milliequivalents of solid Na_2CO_3 = Number of milliequivalents of Na_2CO_3 in solution.

Number of equivalents of solid $Na_2CO_3 = \dfrac{wt.}{its\ eq.\ wt.}$

Number of milliequivalents of solid $Na_2CO_3 = \dfrac{wt.}{its\ eq.\ wt.} \times 1000$

Number of milliequivalents of Na_2CO_3 in solution=

volume of solution (ml) × Normality $(\dfrac{meq}{ml})$

Number of meqts of solid Na_2CO_3 = Number of meqts of Na_2CO_3 in solution.

$\dfrac{wt\ of\ Na_2CO_3}{its\ eq.\ wt.} \times 1000$ = volume of Na_2CO_3 solution × N

$\dfrac{wt\ of\ Na_2CO_3}{53(g/\ meq)} \times 1000 = 250(ml) \times 0.1(meq\ /ml)$

wt of $Na_2CO_3 = \dfrac{53 \times 0.1 \times 250}{1000} = 1.325$ g/ 250ml.

Therefore, 1.325 g of Na_2CO_3 is exactly weighed by sensitive balance and dissolved in 250ml of solution in 250ml size volumetric flask to get 0.1 N of Na_2CO_3 solution. This solution is the standard solution which is prepared from high purity of solid Na_2CO_3.

Ex(2): Show by calculation, how could you prepare 2 litres of 0.2 M NaOH solution from solid NaOH?

The solution:

Mol. wt. of NaOH =23+16+1 =40

Number of moles of solid NaOH = Number of moles of NaOH in solution.

$$\text{Number of millimoles of solid NaOH} = \frac{\text{wt. of NaOH}}{40} \times 1000$$

Number of millimoles of NaOH in solution = volume of solution(ml)×M (mmol/ml)

$$\therefore \quad \frac{\text{wt. of NaOH}}{40} \times 1000 = 2000 \times 0.2$$

$$\text{wt. of NaOH} = \frac{40 \times 0.2 \times 2000}{1000} = 16g$$

Therefore, 16 g of NaOH is weighed by usual balance and dissolved in 2 litres of solution to get 0.2 M. This solution is not standard since NaOH is not primary standard material because:

a) It absorbs water from atmosphere and dissolves in it.

b) It reacts with CO_2 from atmosphere and forms thin layer of Na_2CO_3 surrounding NaOH. Thus NaOH is not pure.

$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Therefore, this solution is standardised with standard solution of an acid such as standard oxalic acid solution using suitable indicator.

4.4.2 Preparation of dilute solutions from concentrated solutions which are commercially available.

The concentrated solutions are always acids or bases kept in bottles carrying some informations such as :percent (w/w), purity, density of the solution or its specific gravity and the formula of the solute and its formula weight. From these informations, one can calculate the concentration of solution which is an approximate because the informations on the bottle are approximate.

In formal, normal and molar concentrations we are dealing with a weight of solute in litre of solution.

Wt. of litre of concentrated solution = volume of solution × its density.

Wt. of solute in litre of solution = volume of solution × density × percentage of solute.

∴ Normality of concentrated solution = $\dfrac{\text{wt. of solute in litre}}{\text{eq. wt. of solute}}$

Therefore, the normality of concd. solution = $\dfrac{1000 \times \text{density} \times \text{percentage}}{\text{eq. wt. of solute}}$

From this concentration, we can calculate the value of concentrated solution that when is diluted to the wanted volume, it gives the required concentration. This concentration is also approximate since we use approximate figures.

Number of milliequivalents of solution before dilution =

Number of milliequivalents of solution after dilution.

$(N_1 V_1)_{\text{before dilution}} = (N_2 V_2)_{\text{after dilution}}.$

V_1 is the wanted volume of concentrated solution when is diluted to V_2 it gives N_2.

Ex(1): Show by calculation how could you prepare 500 ml of 0.1 N H_2SO_4 from its concentrated solution has density of 1.84 g/ml and percentage of acid equals 98% (w/w).?

The solution:

Eq. wt. of $H_2SO_4 = \dfrac{2×1 + 32 + 4×16}{2} = \dfrac{98}{2} = 49$ g/eq

Wt. of H_2SO_4 in litre of solution $= 1000× 1.84× 0.98$ g/lit

Normality of concentrated H_2SO_4 solution $= \dfrac{(1000× 1.84× 0.98) \, g/L}{49 \, g/eq} = 36.8$ eq/lit

Or meq/ml

$N_1V_1 = N_2V_2 \longrightarrow 36.8 × V_1 = 500 × 0.1 \longrightarrow V_1 = \dfrac{500×0.1}{36.8} = 1.4$ ml

Thus, 1.4 ml of coned. sulphuric acid is measured by a graduated cylinder and transferred into a beaker containing 300 ml distilled water with stirring and cooling and then transferred to volumetric flask of 500 ml size. The solution is diluted to the mark with distilled water and stirred vigorously to get homogeneous solution. The same steps are followed when formal and molar concentrations are required with employing formula weight and molecular weight.

Ex(2): Show by calculation how could you prepare 500 ml of 2 M ammonia solution from concentrated solution has specific gravity of 0.9 and percentage of ammonia =27%.?

The solution:

Molarity of concentrated ammonia solution $= \dfrac{1000 × 0.9 × 0.27}{17}$

$= 14.5$ m mol/ml.

$$M_1V_1 = M_2V_2$$

$$14.5 \times V_1 = 2 \times 500 \quad \therefore \quad V_1 = \frac{2 \times 500}{14.5} = 70 \text{ ml.}$$

Therefore, 70 ml of concentrated ammonia solution is measured by a suitable cylinder and transferred to 500 ml size volumetric flask and diluted to the mark with distilled water.

4.4.3 Preparation of dilute solutions from two different concentrated solutions.

Ex(1): Show by calculation how could you prepare a solution of 80% (w/w) H_2SO_4 from two solutions of Sulphuric acid have percentages of 96% (w/w) and 75% (w/w).

The solution:

Crossing arrangement is used for the solution of this example since it is simple and ease for calculation.

96 ⟍   ⟋ 5
    80
75 ⟋   ⟍ 16
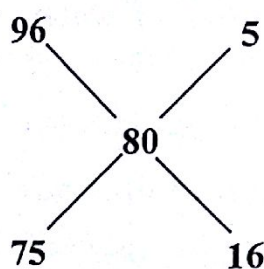
In this example, the lower figure is subtracted from the larger figure irrespective of the mark as shown in left diagram. 96-80=16, 80-75= 5

As the percentage is given (w/w), therefore, 5 weighing units from 96% acid and 16 weighing units from 75% are mixed to get 80%. We can take 10 or 50 from 96% and 32 or 160 from 75%, on condition that the ratio stays as $\frac{5}{16}$.

Ex(2): Show by calculation how could you prepare a litre of sulphuric acid solution has percentage of 50%(w/w) and density of 1.395 g/ml from two solutions of sulphuric acid have percentages 95%(w/w) and 25%(w/w).

The solution:

95   25

50

25   45
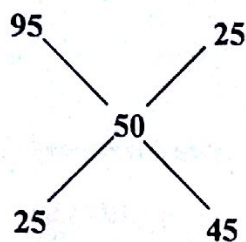
Therefore, 25g of 95% acid is mixed with 45g of 25% acid to get 70g of 50% of acid. But the wanted solution is litre =1000ml

Wt. of litre of the prepared solution =1000×1.395 = 1395g

Therefore, to get litre of 50% of sulphuric acid from two solutions by weighing:
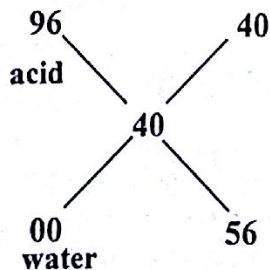
25+45=70 total weight.

$\dfrac{1395×25}{70}$ =498 g from 95% acid

$\dfrac{1395×45}{70}$ =897 g from 25% acid

Total weight =498+897 = 1395 g.

Ex(3): How could you prepare a solution of 40% Nitric acid from 96% nitric acid, if its density equals 1.08 g/ml and the density of water =1g/ml. ?

The solution:

96   40
acid

40

00   56
water

96-40 =56 acid,   40-00 =40 water.

Therefore, 56 g of acid is mixed with 40 g of water to get 40% nitric acid.

$\dfrac{40}{1.08}$ =37 ml of acid , $\dfrac{40}{1}$ =40 ml of water

Therefore, 37 ml of acid is mixed with 40 ml of water to get 40% of acid. Treatment with volumes is simpler than treatment with weight.

Ex(4): How many grams of water should be added to 100 g of ammonia solution/has/percentage of 25% in order to get a solution has percentage of 5% ?

The solution:

25   5
NH$_3$

5
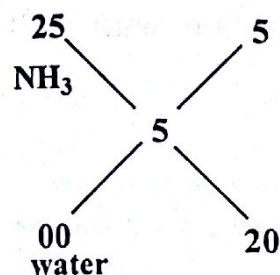
00   20
water

25-5 =20 ammonia,   5-00 =5 water.

Therefore, 5 g of ammonia is mixed with 20 g of water to get 5% of ammonia solution.

But the required weight of water is wanted to be added to 100 ml of ammonia, thus:

$$\frac{100 \times 20}{5} = 400 \text{ g of water should be added to 100 ml of ammonia}$$

to get 5% ammonia.

4.5 Chemical Calculations of Volumetric Titrations.

Chemical calculations which associate with the titration process in volumetric analysis are very significant since they illustrate the idea about the accuracy of titration data which refer to the precision of measurements that lead to accurate results.

The reaction in volumetric analysis should be rapid and complete. The reactions are expressed in balanced equations and from these reactions one can know the ratio of reactants since they involve equivalent amount of the reactants at equivalence point.

Normal concentration gives simple and rapid calculations because they involves equivalent amounts of the reactants. which participate in the titration reactions.

Molar concentrations require some attention and recognition.

For example, if NaOH solution is titrated with HCl solution, there is no difference in using normality or molarity *concentration* because the reaction is performed in 1:1 ratio between NaOH and HCl

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

But the case is different in titration of Na_2CO_3 solution with HCl solution.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

Where two moles of HCl react with one mole of Na_2CO_3. This means that the strength of Na_2CO_3 is twice of HCl. If the molar concentration is used, a precaution should be given to the factor 2 in HCl.

$$(V \times M)_{Na_2CO_3} \neq (V \times M)_{HCl} \quad \textit{(Not equal)}$$

This equality is incorrect *when* if molar concentration is used. Therefore, a factor of 2 should be used at the left side of the above reaction in order to express (correctly) the reaction between Na_2CO_3 and HCl.

$$2(V \times M)_{Na_2CO_3} = (V \times M)_{HCl}$$

But if *when* the normal concentration is employed for both solutions, the following reaction is correct because the *relative* reaction *it* is performed on the basis of equivalents or milliequivalents. *to express the Concentration*

$$(V \times N)_{Na_2CO_3} = (V \times N)_{HCl} \quad \textit{(alway is a Correct relation)}$$

The same treatment is considered in precipitation, oxidation-reduction and complex formation titrations.

4.5.1 Calculations of acid-base titrations or neutralization titrations (one of the products is water).

Ex(1): Calculate the weight of H_2SO_4 in 5 litres if 25 ml of this solution requires 22.5 ml of 0.095 N KOH.

The solution:

Eq. wt. of $H_2SO_4 = \dfrac{2\times1 + 32 + 4\times16}{2} = \dfrac{98}{2} = 49$

No. of meqts of KOH = No. of meqts of H_2SO_4

$\underset{\text{KOH}}{(22.5 \times 0.095)} = \underset{H_2SO_4}{(N \times 25)}$

$N_{H_2SO_4} = \dfrac{22.5 \times 0.095}{25} = 0.0855$ eq/lit

Wt. of H_2SO_4 in 5 litres = N × eq. wt. × $\dfrac{5}{1}$

$= 0.0855 \times 49 \times 5 = 20.9475$ g

Ex(2): A solution of Na_2CO_3 contain 795 mg per litre of solution. Calculate the normality of this solution. What is the volume of H_2SO_4 of 0.1 N that equivalent to 10 ml of Na_2CO_3 solution.

The solution:

$N = \dfrac{0.795 \,g/L}{53 \,g/eq} = 0.015$ meq/ml normality of Na_2CO_3

$\underset{H_2SO_4}{(V\times0.1)} = \underset{Na_2CO_3}{(0.015\times10)}$

$V_{H_2SO_4} = \dfrac{0.015 \times 10}{0.1} = 1.5$ ml H_2SO_4 required to equivalent 10 ml of 0.1 N Na_2CO_3

Ex(3): 30 g of $KHC_2O_4.H_2C_2O_4.2H_2O$ is dissolved in distilled water and completed to a litre. 40 ml of this solution is titrated with KOH which required 20 ml. Calculate the normality of KOH.

The solution:

Eq. wt. $KHC_2O_4.H_2C_2O_4.2H_2O = \dfrac{39+3\times1+4\times12+8\times16+2\times18}{3}$

$= \dfrac{254}{3} = 84.67 \ g/eq$

N of this solution $= \dfrac{30}{84.67} = 0.3543$ eq/lit or meq/ml.

meqts of this acidic solution = meqts of KOH

$\underset{\text{acidic solution}}{(40 \times 0.3543)} = \underset{\text{KOH}}{(20 \times N)} \longrightarrow N_{KOH} = \dfrac{40 \times 0.3543}{20} = 0.7086$ meq/ml.

Ex(4): 10 ml of vinegar has density of 1.055 g/ml and requires 39.82 ml of 0.225 N of a base to reach equivalence point. Calculate the percentage of acetic acid in vinegar (w/w).

The solution:

Wt. of vinegar sample = volume × density

$$= 10 \times 1.055 = 10.55 \text{ g}$$

No. of meqts. of vinegar solution = No. of meqts. of base.

$$0.255 \times 39.82 = N_{CH_3COOH} \times 10$$

$$N_{CH_3COOH} = \dfrac{0.255 \times 39.82}{10} = 1.01541 \text{ eq/lit} \\ \text{or meq/ml}$$

wt. of acetic acid in vigenar $= N \times$ eq. wt. $\times \dfrac{10}{1000}$

Eq.wt of $CH_3COOH = \dfrac{2 \times 12 + 2 \times 16 + 4 \times 1}{1} = \dfrac{60}{1} = 60$ g/eq

$= 1.01541 \times 60 \times \dfrac{10}{1000} \longrightarrow = 0.6092 \text{ g}$

% of CH3COOH in vinegar $= \dfrac{0.6092}{10.55} \times 100 = 5.77 \%(w/w)$

Ex(5): 0.3542 g of Na_2CO_3 was dissolved in water and titrated with HCl which consumed 30.32 ml of the acid. Calculate the normality of HCl solution. *molarity*

The solution:

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

$\therefore$ 2×No. of mmols of Na_2CO_3 = No. of mmols of HCl *(at the end point)*
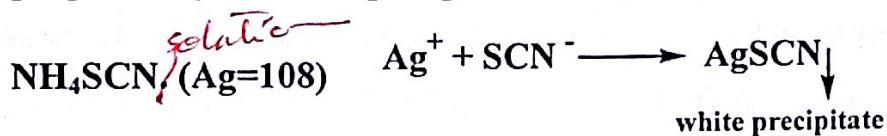
$$2 \times \frac{0.3542}{106} \times 1000 = M_{HCl} \times 30.32$$

M_{HCl} = 2.21 mol / lit or mmol / ml

4.5.2 Calculations of precipitation titrations.

In precipitation titrations, one of the products is slightly soluble salt called precipitate.

Ex(1): Calculate the percentage of silver in a silver alloy if a solution prepared by dissolving 0.3g of the alloy requires 23.80ml of 0.1N of

NH_4SCN *solution* (Ag=108) $Ag^+ + SCN^- \longrightarrow AgSCN\downarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ white precipitate

The solution:

No. of meqts. of Ag^+ = No. of meqts of SCN^- *(at the end point)*

$$\frac{\text{wt. of silver}}{\text{its eq. wt.}} \times 1000 = (V \times N)_{SCN^-} \longrightarrow \frac{\text{wt. of silver}}{108} \times 1000 = 23.80 \times 0.1$$

$$\text{wt. of silver} = \frac{108 \times 0.1 \times 23.80}{1000} = 0.257 \text{ g}$$

$$\therefore \quad \% \text{ Ag} = \frac{0.257}{0.3} \times 100 = 85.67 \%$$

where

Ex(2): Find the weight of $BaCl_2$ in 250 ml of solution were 40 ml in excess of 0.102 N $AgNO_3$ was added to 25 ml of $BaCl_2$. The excess of $AgNO_3$ solution was titrated with 0.098 N SCN^- *and required 15 ml to reach the end point*

The solution:

$$BaCl_2 + 2AgNO_3 \longrightarrow Ba(NO_3)_2 + 2AgCl$$

$$AgNO_3 + SCN^- \longrightarrow AgSCN\downarrow + NO_3^-$$

No. of meqts of $AgNO_3$ = No. of meqts of SCN^- + No. of meqts of $BaCl_2$.

$$\underset{AgNO_3}{(0.102 \times 40)} = \underset{BaCl_2}{(N \times 25)} + \underset{SCN^-}{(0.098 \times 15)}$$

$$1.47 + 25 \, N = 4.08$$

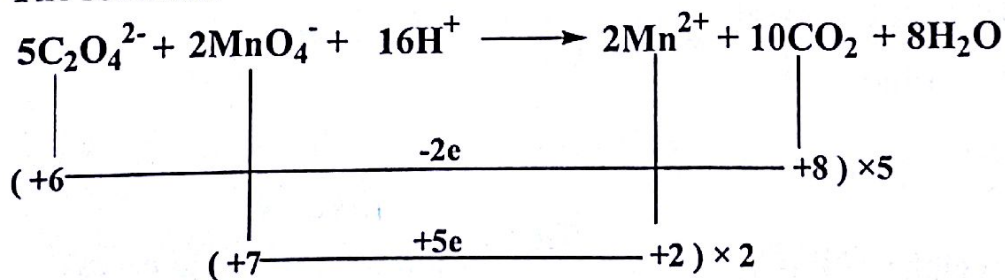$$N = \frac{2.61}{25} = 0.1044 \text{ meq / ml normality of } BaCl_2 \text{ solution.}$$

$$\text{Wt. of } BaCl_2 \text{ in 250 ml} = N_{BaCl_2} \times \text{its eq. wt.} \times \frac{250}{1000}$$

$$= 0.1044 \times 104.17 \times \frac{250}{1000} \longrightarrow = 2.72 \text{ g } BaCl_2 \text{ / 250 ml.}$$

4.5.3 Calculation of oxidation-reduction titrations.

These titrations involve the reactions between oxidant and reductant which subject transferring of electrons from reductant to oxidant.

Ex(1): A sample of $Na_2C_2O_4$ weighs 0.2734 g is dissolved in water acidified with dilute H_2SO_4 and titrated at 70^oC with $KMnO_4$ solution, which requires 42.68 ml. The titration exceeds the equivalence point and the excess of $KMnO_4$ is back titrated with 0.1024 N oxalic acid which requires 1.46ml. Calculate the normality of $KMnO_4$ solution.

The solution:

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

$(+6 \underline{\hspace{1cm}} -2e \underline{\hspace{1cm}} +8) \times 5$

$(+7 \underline{\hspace{1cm}} +5e \underline{\hspace{1cm}} +2) \times 2$

$$\text{Eq. wt. of } Na_2C_2O_4 = \frac{2 \times 23 + 2 \times 12 + 4 \times 16}{2} = 67$$

No. of meqts of $KMnO_4$ = No. of meqts of $Na_2C_2O_4$ + No. of meqts of $H_2C_2O_4$
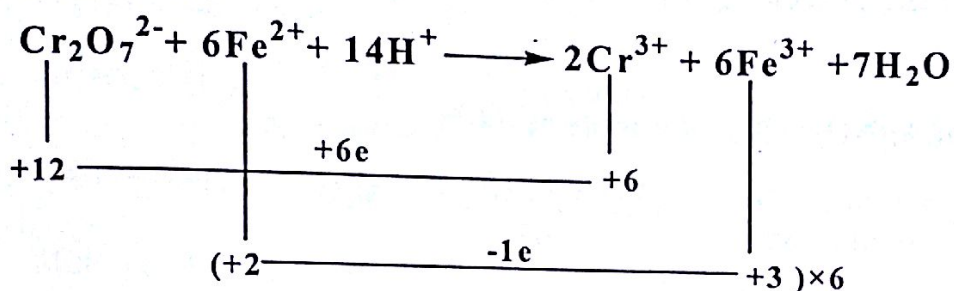
$$N_{KMnO_4} \times 42.68 = \frac{0.2734}{67} \times 1000 + 1.46 \times 0.1024$$

$$N_{KMnO_4} = \frac{4.2301}{42.68} = 0.09911 \text{ meq/ml or eq/lit}$$

Ex(2): A sample of Iron ore/which weighs 0.6038 g was dissolved in an acid and Fe^{3+} is reduced to Fe^{2+} and titrated with 0.1073 N $K_2Cr_2O_7$ which requires 38.42 ml. Calculate the percentage of Fe in the sample and express the percentage as FeO, Fe_2O_3 and Fe_3O_4. Atomic wt. of Fe =56.

The solution:

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

$$+12 \underset{}{\overset{+6e}{\rule{4cm}{0.4pt}}} +6$$

$$(+2 \underset{}{\overset{-1e}{\rule{4cm}{0.4pt}}} +3) \times 6$$

No. of meqts of Fe^{2+} = No. of meqts of $K_2Cr_2O_7$

$$\frac{\text{wt. of Fe}}{\text{its eq. wt.}} \times 1000 = (V \times N)_{K_2Cr_2O_7}$$

$$\frac{\text{wt. of Fe}}{56} \times 1000 = 38.42 \times 0.1073 \longrightarrow \text{wt. of Fe} = \frac{56 \times 38.42 \times 0.1073}{1000} = 0.231g$$

$$\% \text{ of Fe} = \frac{0.231}{0.6038} \times 100 = 38.23 \%$$

$$\% \text{ as FeO} = 38.23 \times \frac{FeO}{Fe} = 38.23 \times \frac{72}{56} = 49.15\%$$

$$\% \text{ as Fe}_2O_3 = 38.23 \times \frac{Fe_2O_3}{2Fe} = 38.23 \times \frac{160}{112} = 54.61\%$$

$$\% \text{ as Fe}_3O_4 = 38.23 \times \frac{Fe_3O_4}{3Fe} = 38.23 \times \frac{232}{168} = 52.71\%$$

4.5.4 Calculations in complex formation titrations

In these titrations, a stable complex is formed which is exploited in the determination of most metal ions with EDTA as a ligand.

Ex(1): 25.42 ml of 0.045 M $AgNO_3$ is required to titrate a sample of impure KCN which weighed 0.3123 g according to the following reaction:

$$Ag^+ + 2CN^- \longrightarrow Ag(CN)_2^- \quad \longleftarrow \cdots \cdots \text{ complex ion}$$
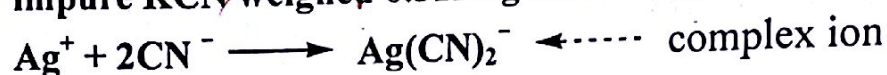
Calculate the percentage of KCN in the sample.

The solution:

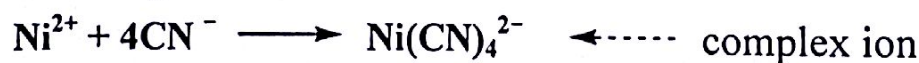$2 \times$ No. of mmols of $AgNO_3$ = No. of mmols of KCN

$$2 \times 0.045 \times 25.42 = \frac{\text{wt. of KCN}}{\text{its mol. wt.}} \times 1000 = \frac{\text{wt. of KCN}}{65} \times 1000$$

$$\text{wt. of KCN} = \frac{65 \times 2 \times 0.045 \times 25.42}{1000} = 0.1488 \text{ g}$$

$$\% \text{ KCN} = \frac{0.1488}{0.3123} \times 100 = 47.65 \%$$

Ex(2): 25 ml of Ni^{2+} solution requires 0.521 g of KCN according to the following reaction:

$$Ni^{2+} + 4CN^- \longrightarrow Ni(CN)_4^{2-} \quad \longleftarrow \cdots \cdots \text{ complex ion}$$

Calculate the molarity of Ni^{2+} solution.

The solution:

1 mol of Ni^{2+} requires 4 mols of KCN in order to get the above reaction. The strength of Ni^{2+} is four times greater than KCN.

$\therefore 4 \times$ No. of mmols of Ni^{2+} = No. of mmols of KCN.

$$4 \times 25 \times M_{Ni^{2+}} = \frac{\text{wt. of KCN}}{\text{its Mol. wt.}} \times 1000 \longrightarrow 4 \times 25 \times M_{Ni^{2+}} = \frac{0.521}{65} \times 1000$$

$$M_{Ni^{2+}} = \frac{0.521 \times 1000}{4 \times 25 \times 65} = 0.08 \text{ mol / lit}$$

$$\text{or } 0.08 \text{ mmol / ml}$$

Ex(3): 3 g of EDTA (disodium) is dissolved in one litre. Calculate the volume of 0.05 M Mg^{2+} solution required to react with 25 ml of EDTA solution.

The solution:

The ratio of reaction is $1\ Mg^{2+} : 1$ EDTA

EDTA is ethylenediamine tetra acetic acid abbreviated as $Na_2H_2Y.2H_2O$ which is disodium salt. Also, it is abbreviated as EDTA and has the following formula.

$$HOOCCH_2 \diagdown \qquad \overset{H}{\underset{|}{C}} \quad \overset{H}{\underset{|}{C}} \qquad \diagup CH_2COONa$$
$$N-\underset{|}{C}-\underset{|}{C}-N \qquad\qquad .2H_2O$$
$$NaOOCCH_2 \diagup \qquad \underset{H}{} \quad \underset{H}{} \qquad \diagdown CH_2COOH$$

Mol. wt. of EDTA $=2{\times}23 +8{\times}16 +14{\times}2 +10{\times}12 +2{\times}18 +14{\times}1 = 372$

Molarity of EDTA $=\dfrac{\text{wt. per litre}}{\text{its Mol. wt.}} =\dfrac{3}{372} = 0.0081$ mol/lit.

Mg^{2+} reacts with EDTA in the ratio 1:1 $\sim Mg^{2+} + EDTA \longrightarrow Mg\text{-}EDTA$

No. of mmols of EDTA = No. of mmols of Mg^{2+}

$$\underset{EDTA}{(25{\times}0.0081)} = \underset{Mg^{2+}}{(V{\times}0.05)}$$

$$\underset{Mg^{2+}}{V} =\dfrac{25{\times}0.0081}{0.05} = 4.05\text{ml}$$

4.6 Problems:

1- Show by calculations how could you prepare the following solutions:

a) 525 ml of 0.4 F $BaCl_2$ from solid $BaCl_2.2H_2O$.

b) 2.30 litres of 0.2 M K^+ from solid K_2SO_4.

c) 100 ml of 0.1 F $AgNO_3$ from a solution that was 0.441 F in the salt.

d) 3 litres of a solution containing 10 ppm NH_3 from a 0.116 F solution of NH_3.

2- Show by calculations how could you prepare the following solutions:

a) 750 ml of 0.172 F $K_2Cr_2O_7$ from the solid salt.

b) 50 litres of a solution that is 0.1 F in Na_2SO_4 from solid Na_2SO_4.

c) 2 litres of a solution that is 0.015 M in Na^+ from solid NaCl.

d) 20 litres of a solution that is 0.202 M in Na^+ from a 2.42 F solution of Na_2SO_4.

3- Show by calculations how could you prepare 800 ml of 0.20 F HNO_3 from concentrated HNO_3 has specific gravity of 1.42 and percentage is 69% HNO_3 (w/w).

4- A solution of concentrated HCl has specific gravity of 1.185 and percentage is 36.5 % (w/w) HCl. Explain how 1.50 litres of approximately 0.3 F HCl should be prepared from the concentrated solution.

5- Describe the preparation of 400 ml of 6 F H_3PO_4 from the commercial solution is 85%(w/w) H_3PO_4 and has density of 1.69 g/ml.

6- Describe the preparation of 200 ml of 3 F H_2SO_4 from the concentrated solution which is 95%(w/w) H_2SO_4 and density of 1.84 g/ml.

7- Calculate the formal concentration of 12%(w/w) $CuSO_4$ solution which has density of 1.13 g/ml.

8- Calculate the formal concentration of solution that is 25% in H_2SO_4 (w/w) and has specific gravity of 1.19.

9- A solution was prepared by dissolving 1.68 g of $K_4Fe(CN)_6$ in water and diluting exactly to 500 ml. Calculate:

    a) The formal concentration of $K_4Fe(CN)_6$.

    b) The molar concentration of K^+ assuming complete dissociation.

    c) The weight-volume percent of $K_4Fe(CN)_6$.

    d) The weight-weight percent of $K_4Fe(CN)_6$ if the density of solution = 1.008 g/ml.

    e) The number of moles $Fe(CN)_6^{4-}$ in 16 ml of the solution.

10- Calcium concentration in sea water is 4×10^2 ppm, calculate its formal concentration if the average density of sea water =1.024 g/ml.

11- Magnesium concentration in human blood serum is 27 ppm, calculate its molar concentration.

12- Exactly 46.32 ml of NaOH solution is used to titrate 1200 mg sample of primary standard potassium acid phthalate (KHP, fw =204.2), calculate the normality of NaOH solution.

13- Exactly 24.69 ml of HCl solution is required to titrate a 278 mg sample of the primary standard tris(hydroxyl-methyl) amino ethane according to the following reaction:

$$HCl + (CH_2OH)_3CNH_2 \longrightarrow (CH_2OH)_3C\overset{+}{N}H_3Cl^-.$$

Calculate the molarity of HCl.

14- Calculate the percentage purity of 500 mg sample of impure sodium carbonate that requires 22 ml of 0.18 N HCl for complete neutralization.

15- An impure 1 g sample of arsenious acid (H_3AsO_3) is oxidised to H_3AsO_4 by titration with 45 ml of 0.08 N iodine. Calculate the percentage of H_3AsO_3 (fw=125.9) and percentage of As.

16- 10 ml of a sample of NaCl solution is diluted to 50 ml. A 20 ml of this solution is titrated with 3.923 ml of 0.011 M $AgNO_3$ solution. Calculate the molarity of the original NaCl solution.

17- 50 ml of sample of chloride requires 15.5 ml of 0.011 M $AgNO_3$ in precipitation titration. Calculate the percentage of chloride (Cl^-) $\left(W/_V\right)$.

18- 20 ml of 0.05 M EDTA is added to 700 mg of iron(II). The excess of EDTA is back titrated with 5.08 ml of 0.042 M Cu^{2+} solution. Calculate the percentage of Fe^{2+} as Fe_2O_3 in the sample.

19- Tin(II) is titrated with dichromate according to the equation:
$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O .$$

Calculate the weight of tin(II) in a sample that requires 20 ml of 0.1 M $Cr_2O_7^{2-}$.

20- A 550 mg sample of aluminum is analysed by adding 50 ml of 0.05 M EDTA. The excess of EDTA is back titrated with 14.4 ml of 0.048M zinc solution. Calculate the percentage of aluminum in the sample.