Unit 2: Volumetric Analysis

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Unit 2: Volumetric Analysis

Syllabus

- Different ways of expressing the concentration of solutions
  i. Molarity, ii. Normality iii. Molality iv. Gram /Litre v. Percentage
- Titration : i. acid-base titration ii. Redox titration
- Primary standard substances, primary standard solution, secondary standard solution, end point, equivalence point, neutral point, indicators
- Derivation of normality equation
- Relation between normality and molarity
- Selection of indicators in acid-base titration and pH curve
- Solving related numerical problems

Some important terms, concepts and formulae

1. A solution with known strength is called standard solution.
2. A solution without a known strength is unknown solution.
3. g/L is called strength in general.
4. Weight of solute in gram present in one litre of it's solution is called gram per litre. i.e.

$$\text{gram per litre (g/L)} = \frac{\text{Wt. in gram}}{\text{Volume in litre}}$$

5. Normality is defined as number of gram equivalent of a solute present in one litre of it's solution. i.e.

$$\text{Normality (N)} = \frac{\text{No. of gram equivalent of solute}}{\text{Volume of solution in litre}}$$

6. Normality is related to g/L as

$$\text{g/L} = \text{Normality (N)} \times \text{Equivalent wt. of solute.}$$

7. A normal solution has normality 1N and a decinormal solution has normality 0.1N.
8. Molarity is defined as number of moles of solute present in one litre of it's solution. i.e.

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$$

9. Molarity is related to gram per litre as:

$$\text{gram per litre (g/L)} = \text{Molarity (M)} \times \text{Molecular weight of solute}$$

10. Normality and molarity are related as.

$$\text{Normality (N)} = \text{Molarity (M)} \times \text{basicity of acid}$$

or, $$\text{Normality (N)} = \text{Molarity (M)} \times \text{acidity of base.}$$

11. A solution prepared from primary standard substance is called primary standard solution.
12. A primary standard substance is not hygroscopic, not toxic, easily available in pure state and has high molecular weight.
13. The point at which the indicator changes it's colour at the time of titration is called end point.
14. The point of titration at which one gram equivalent of an acid is completely neutralized by one gram equivalent of a base is called equivalence point.
15. The difference between end point and equivalence point is called titration error.

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples. After doing the solved examples, try to solve the other similar questions independently.

Subject Matter

Very Short Questions-Answers

Q.1. Define Normal solution.

Ans: A solution containing one gram-equivalent of the solute in one litre of its solution is known as Normal (N) solution. For example: If 40 g NaOH is present in 1000 cc (1 litre) of its solution, the solution is known as normal (N) solution.

Q.2. Define acidity of a base and basicity of an acid.

Ans: **Acidity of a base:** Acidity of a base is numerically equal to the number of hydroxide ion in a base or twice the number of oxygen present as oxide per molecule of a base. E.g. Acidity of either CaO or $Ca(OH)_2$ is 2.

Basicity of an acid: Basicity of an acid is given by the number of replaceable hydrogen atoms present in a molecule of that acid. For example, basicity of HCl is 1 and basicity of H_2SO_4 is 2.

Q.3. What is meant by standard solution and primary standard substance?

Ans: **Standard solution:** A solution of known strength is known as standard solution i.e. if the amount of solute is known in a given volume of solution, the solution is known as standard solution. For example: 250 mL of N/10 NaOH is a standard solution.

Primary standard: The chemicals which are non deliquescent (non-hygroscopic), non-volatile and that can be accurately weighed out so as to prepare it's standard solution, are known as primary standards. e.g.: Na_2CO_3, $K_2Cr_2O_7$, $(COOH)_2$ etc.

The strength of the solution of primary standard substances doesn't vary when kept for a few days.

Q.4. What is an indicator?

Ans: Indicator is the third substance used in titration to indicate the end point or neutral point of the titration. It indicates the completion of the reaction during titration by changing its colour with the change in the pH of the solution at equivalence point, e.g. phenolphthalein, methyl orange, etc.

Q.5. Distinguish end point and equivalence point.

Ans: A particular stage during titration where the change in colour of indicator, indicates completion of reaction is known as end point. It is also called practicle end point.

We know different substances react together in their equivalent proportion. So, the point or stage at which one gram equivalent of a substance reacts completely with one gram equivalent of another substance is known as equivalence point. It is also called theoretical end point.

Q.6. What do you mean by titration error?

Ans: The difference between end point and equivalence point is titration error. During titration we should minimize the titration error as much as it is possible by selecting a suitable indicator.

Q.7. What mass of Na_2CO_3 is required to make 50cc of its seminormal solution?

Soln: Given, Volume of solution (V) = 50cc $= \frac{50}{1000} = 0.05$ L

Strength of Na_2CO_3 solution (N) $= \frac{1}{2}$N

Mass of Na_2CO_3 (w) = ?

We know that,

$$\text{Normality (N)} = \frac{\text{No. of gm-equivalent of solute}}{\text{volume of solution in Litre}}$$

$$= \frac{\text{weight of solute/ Equivalent weight of solute}}{\text{Volume of solution in Litre}}$$

or, $0.5 = \frac{w/53}{0.05}$ [$\because$ Equivalent weight of $Na_2CO_3 = 53$]

or, $w = 0.5 \times 0.05 \times 53 = 1.325$ g

Hence, 1.325g of Na_2CO_3 is needed to prepare, 50cc of its seminormal solution.

Q.8. ***Write an example of a redox titration. Why is it called so?***

Ans: The standardization of acidic $KMnO_4$ solution with the help of standard oxalic acid solution can be regarded as an example of redox titration. The reaction is given below:

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

It is called so because the reaction involved here is a redox reaction. Here $KMnO_4$ is reduced to $MnSO_4$ whereas $C_2H_2O_4$ is oxidized to CO_2 and H_2O.

Q.9. ***A partially hydrated sodium carbonate $Na_2CO_3.H_2O$ weighing 0.31 g is added to 100 mL of 0.05 N H_2SO_4 solution will the resulting solution be neutral, acidic or basic?***

Ans: Let's calculate the amount of H_2SO_4 (x) present in 100 mL of it's 0.05 solution.

$$\text{Eq. wt of } H_2SO_4 = \frac{2 \times 1 + 32 + 4 \times 16}{2} = \frac{98}{2} = 49$$

Normality = 0.05 N

Volume of H_2SO_4 = 100 mL = 0.1 L

$$\text{We know, normality} = \frac{\text{No. of gram equivalent}}{\text{volume in L}}$$

or, $0.05 = \frac{x/49}{0.1}$

$\therefore$ $x = 0.245$ g

Now, H_2SO_4 reacts with sodium carbonate as:

$$\underset{\substack{1\text{ mol}\\124\text{ g}}}{Na_2CO_3.H_2O} + \underset{\substack{1\text{ mol}\\98\text{ g}}}{H_2SO_4} \rightarrow Na_2SO_4 + CO_2 + 2H_2O$$

i.e. 98 g of H_2SO_4 needs 124 g $Na_2CO_3.H_2O$ for complete reaction.

or, 0.245 g of H_2SO_4 needs $\frac{124}{98} \times 0.245$ g $Na_2CO_3.H_2O$ for complete reaction.

$= 0.31$ g

Since, the amount of $Na_2CO_3 . H_2O$ needed is same as the amount of $Na_2CO_3.H_2O$ added, the solution will be neutral.

Q.10. ***5g of a diacidic base is completely neutralized by 50 mL of 2N HCl. Find the molecular weight of the base.***

Soln: Given,

Acidity of the base = 2

Wt. of base neutralized = 5g

Volume of acid used = 50 mL

Strength of acid used = 2N

We have,

50 mL of 2N HCl completely neutralized 5 g of the base.

or, 1000 mL of 2N HCl completely neutralized $\frac{5}{50} \times 1000$ g the base.

or, 1000 mL of 1N HCl completely neutralized $\frac{5 \times 1000}{50 \times 2}$ g the base.

$= 50$ g the base

But 1000 mL of 1N HCl is equivalent to 1gram-equivalent of HCl and we also know that 1 gram equivalent of an acid completely neutralizes 1 gram equivalent of a base. Thus, equivalent weight of the base is 50.

So, its molecular weight = Equivalent wt. × acidity = 50 × 2 = 100.

Hence, molecular weight of the diacidic base is 100.

Q.11. ***If 5.85 g sodium chloride is present in 100 mL solution, what will be its molarity?***

Sol^n: 100 mL of this solution contains 5.85 g NaCl.

so, 1000 mL of this solution contains 58.5 g NaCl.

$\therefore$ Strength (g/L) = 58.5 g/L.

Now, Molarity related to g/L is as:

g/L = Molarity × Molecular weight.

$$\therefore \quad \text{Molarity} = \frac{\text{g/L}}{\text{molecular weight}}$$

$$= \frac{58.5}{58.5} \quad [\because \text{Mol.wt. of NaCl is } 58.5]$$

$$= 1\text{M}.$$

$\therefore$ The molarity of 100 mL NaCl solution containing 5.85 g of it is 1M.

Q.12. ***Calculate the molarity of a solution containing 1 g of NaOH in 250 mL of it's aquous solution.***

Ans: The aquous solution of NaOH contains 1g NaOH in 250 mL of its solution.

So, it's strength in gram per litre is $\frac{1}{250/1000} = 4\ \text{gL}^{-1}$

Now, we have,

Strength of NaOH = 4gL^{-1}

Molecular wt. of NaOH = 40

Molarity of NaOH (M) = ?

We know, molarity (M) = $\frac{\text{gL}^{-1}}{\text{Mol. wt}} = \frac{4}{40} = 0.1$ M.

Hence, the NaOH solution is 0.1 M.

Q.13. ***What volume of 5N HCl should be diluted to make one litre of it's normal solution?***

Soln: Given,

Initial strength (S_1) = 5N　　Final strength (S_2) = 1 N

Initial volume (V_1) = x cc　　Final volume (V_2) = 1000 cc

We know, according to normality equation

$$V_1 \times S_1 = V_2 \times S_2$$

or, $x \times 5 = 1 \times 1000$

or, $x = \frac{1000}{5} = 200$ cc.

Hence, the value of x = 200 cc. i.e. initially 200 cc of 5 N HCl should be taken and diluted to 1L to get 1N HCl solution.

Short Questions-Answers

Q.14. How is a suitable indicator selected for a particular titration?

Ans: The main purpose of selecting a suitable indicator is to find out the end-point as much nearer as possible to the equivalent point. This will minimize the titration error to its possible lowest. An indicator indicates the end point by change in its colour but all of them do not do so at the same pH range. In fact, they all have their own specific pH range. For example, phenolphthalein changes its colour at pH range of 8 to 9.5 and methyl orange at pH range 3 to 4.5. The pH at the end point of a titration depends upon the nature of titre and titrant so, the indicator should be selected properly as to coincide that end point with equivalence point. This can be done as follows:

(i) **Strong acid and strong base titration:** In strong acid-base titration pH value changes before and after the equivalent. In this type of titration pH value changes very slowly to begin with but at the neutral point the pH value changes sharply on the addition of very small amount of base. Therefore, any indicator either methyl orange or phenolphthalein can be used.

e.g.: $NaOH + HCl \longrightarrow NaCl + H_2O$

(ii) **Strong acid and weak base titration:** When a strong acid like HCl is titrated against a weak base like NH_4OH or Na_2CO_3, the salt produced at the equivalent point will be slightly acidic due to hydrolysis.

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

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

For such reactions, the pH at the equivalent point becomes less than 7 and, for this, indicator used should give the colour change in acidic medium, and thus, methyl orange is used as indicator and its colour range being 4.5 to 6.5.

(iii) **Weak acid and strong base:** Considering the reaction between weak acid and strong base, like acetic acid with sodium hydroxide.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$CH_3COONa + H_2O \longrightarrow CH_3COOH + NaOH$$

There is very little change in the pH value until the neutral point is reached. When the pH value suddenly alters from 6.5 to 10 for the solution at the end point, the solution becomes slightly alkaline due to the hydrolysis of salt produced. For this, phenolphthalein is proper indicator.

(iv) **Weak acid and weak base titration:** In this type of titration no sharp change in the pH value takes place i.e. pH value remains practically constant around the equivalent point of this type of reactions because of the formation of a buffer. Therefore, no indicator is required for weak acid and weak base titration. Thus, a suitable indicator is selected on the basis of the nature of the reactions or nature of acid-base titration.

Q.15. 2.1 g of a sample containing NaOH and Na_2CO_3 was dissolved in water and solution was made upto 250 mL. A 20 mL of this solution required 40 mL of N/10 H_2SO_4 for complete neutralization. Calculate the percentage weight of NaOH and Na_2CO_3.

Soln: Let the wt. of Na_2CO_3 = xg

$\therefore$ wt. of NaOH = (2.1 – x) g

Now, (i) Na_2CO_3 reacts with H_2SO_4 as

$$\underset{\substack{1 mol \\ 106 g}}{Na_2CO_3} + \underset{\substack{1 mol \\ 98 g}}{H_2SO_4} \longrightarrow Na_2SO_4 + CO_2 + H_2O$$

106 g Na_2CO_3 completely reacts with 98 g of H_2SO_4.

x g Na_2CO_3 completely reacts with $\frac{98}{106} \times x$ g of H_2SO_4.

Similarly, (ii) NaOH reacts with H_2SO_4 as

$$\underset{\substack{2 mol \\ 80 g}}{2NaOH} + \underset{\substack{1 mol \\ 98 g}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$$

80 g NaOH completely reacts with 98 g H_2SO_4

or, (2.1–x) g NaOH completely reacts with $\frac{98}{80} \times (2.1 - x)$ g H_2SO_4

or, Total amount of H_2SO_4 required $= \frac{98x}{106} + \frac{98(2.1 - x)}{80}$ ...(1)

Now let us find the amount of H_2SO_4 in 40 mL of it's N/10 solution.

20 mL of the solution required 40 mL of N/10 H_2SO_4

or, 250 mL of the solution required $\frac{40}{20} \times 250$ mL of N/10 H_2SO_4

$= 500$ mL of N/10 H_2SO_4.

Let, a gram of H_2SO_4 is present in 500 mL of N/10 H_2SO_4.

or, $\text{Normality} = \frac{\text{wt. in g / Eq. wt.}}{\text{volume in L}}$

or, $0.1 = \frac{a/49}{500/1000}$ [$\because$ Eq. wt. of H_2SO_4 is 49.]

or, $a = 2.45$ g. .....(2)

Now, equating equation (1) and (2), we get,

$$\frac{98x}{106} + \frac{98\,(2.1 - x)}{80} = 2.45$$

or, $80 \times 98x + 106 \times 98\,(2.1 - x) = 2.45 \times 80 \times 106$

or, $7840x + 21814.8 - 10388x = 20776$

or, $-2548x = -1038.8$

$\therefore$ $x = \frac{1038.8}{2548} = 0.4077$g.

$\therefore$ % of $Na_2CO_3 = \frac{0.4077}{2.1} \times 100 = 19.4\%$

and % of NaOH $= (100 - 19.4) = 80.6\%$

Q.16. ***What is meant by titration error? In a titration of 20.0 mL of aquous solution of NaOH with 0.10 N HCl, the observed end point is 22.7 mL, whereas the equivalence point is 22.5 mL. Calculate the percentage error in the mass of hydrochloric acid per litre of the analyte for this titration.***

Ans: Almost in every titration, the volume of the titrant added to note the end point is slightly higher than the volume required to react at equivalence point. This difference in volume or mass between the equivalence point and the end point is called as titration error.

In volumetric methods, the titration error, E_t is given by:

$$E_t = V(end) - V(equ.)$$

Where, $V(end) = Vol^m$ of titrant at end point

$V(equ.) = Vol^m$ of titrant at equivalent point

Numerical

The normality of NaOH as per the end point is

$$= \frac{22.7 \times 0.10\ N}{20.0} = 0.1135\ N$$

The mass of HCl per litre = 0.1135 × 36.45 g = 4.1371 g

Where, 36.45 = Equivalent mass of HCl.

Similarly, the mass of HCl per litre as per the equivalence point is

$$= \frac{22.5 \times 0.10\ N}{20.0} \times 36.45\ g$$

$$= 4.1006\ g$$

$$\%\ \text{error in mass per litre} = \frac{(4.1371 - 4.1006) \times 100}{4.1006}$$

$$= 0.9\%$$

Q.17. ***How does a decimolar solution differ from decinormal solution. 20cc of an alkali solution is mixed with 8.0cc of 0.75N acid solution and for complete neutralization, it further required 15cc of 0.8N acid solution. Find the strength of the given alkali solution.***

Ans: A decinormal solution contains $1/10^{th}$ gram equivalent of a solute in one litre of its solution whereas a decimolar solution contains $1/10^{th}$ gram mole of a solute in one litre of its solution. Similarly, the normality of a decinormal solution is 0.1N and molarity of a decimolar solution is 0.1M respectively.

Volume of alkali (V) = 20cc

Normality alkali (N) = ?

Volume of acid 1 (V_1) = 8.0cc

Normality acid 1 (N_1) = 0.75N

Volume of acid 2 (V_2) = 15cc

Normality acid 2 (N_2) = 0.8N.

Now, we know that for complete neutralization,

Total gram-equivalent of alkali = Total gm-equivalent of acid

or, $V \times N = V_1 \times N_1 + V_2 \times N_2$

$$\therefore \quad N = \frac{V_1 \times N_2 + V_2 \times N_2}{V}$$

$$= \frac{8.0 \times 0.75 \times 15 \times 0.8}{20} = 0.8\ N$$

$\therefore$ Strength of that alkali solution in normality = 0.8N.