Lec. 3

Volumetric Analysis

Titration: A method for a quantitive analysis of a substance by an essentially complete reaction in solution with a measured quantity of a reagent of known concentration

Equivalence point: The point in a titration at which one reactant has been exactly consumed by addition of the other reactant

End point: The point in a titration at which the indicator signals that amount of the first reactant has been added to the second reactant

Types of volumetric analysis(titration)

1. Acid - base titration (neutralization titration)
2. oxidation - reduction titration (redox titration)
3. Precipitation titration
4. Complexemetric titration

Acid-base titration

An acid-base titration is the determination of the concentration of an acid or base by exactly neutralizing the acid or base with an acid or base of known concentration. This allows for quantitative analysis of the concentration of an unknown acid or base solution. It makes use of the neutralization reaction that occurs between acids and bases.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$H^+ + OH^- \rightarrow H_2O$$

The key equipment used in a titration are:

- Burette
- White tile - used to see a colour change in the solution

- Pipette
- pH indicator (the one used varies depending on the reactants)
- Erlenmeyer flask (Conical flask)
- Titrant or titrator (a standard solution of known concentration, a common one is aqueous sodium carbonate)
- Analyte or titrand (solution of unknown concentration)

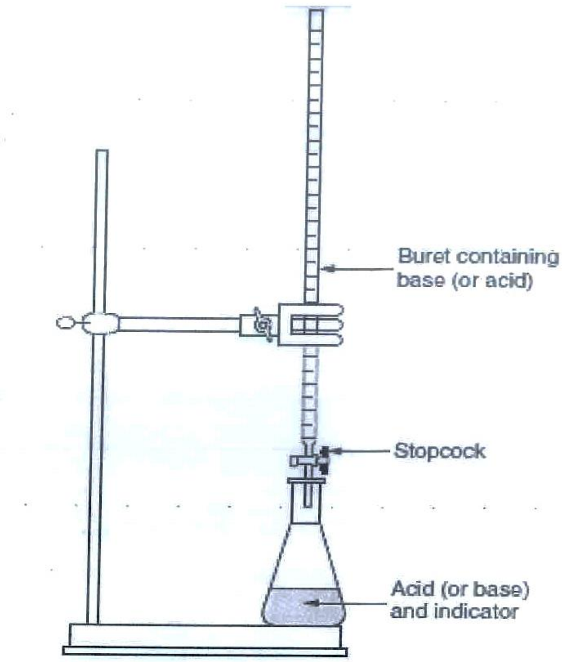

figure : General acid–base titration set-up

Acid-Base Indicator Definition

Definition: An acid-base indicator is either a weak acid or weak base that exhibits a color change as the concentration of hydrogen (H^+) or hydroxide (OH^-) ions changes in an aqueous solution.

Also Known As: pH indicator

Examples:

Thymol Blue, Phenol Red and Methyl Orange are all common acid-base indicators. Red cabbage can also be used as an acid-base indicator.

Standard solution

Is one which contains knows weight of the reagent in a definite volume of the solution. The weight of the substance to be determined is then calculated laws of a chemica) from the volume of the standard solution and the known equivalence. The ideal standard solution for a volumetric method will

1- Be sufficiently stable it is necessary to determine it conc.

2- React rapidly with analyte

Desirable properties of standard material

1- Absence of hydrate water so that the composition does not change witli variation in relative humidity.

2- Stability in air.

3- Ready availability at modest cost.

4- Reasonable solubility in the titration medium.

5- High purity.

6- Reasonable large formula weight so that the relive error associated with weighing is minimized.

Buffer solutions

A buffer is an aqueous solution consisting of a mixture of a weak acid and itsconjugate base or a weak base and its conjugate acid. Its pH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent changes in the pH of a solution. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications.

Biochemical buffers :- Phosphate and bicarbonates are important in biochemical buffers. The phosphate system, which acts in the cytoplasm of all cells, consist of $H_2PO_4^{-1}$ as a proton donor and HPO_4^{-2} as a proton acceptor

$$H_2PO_4^{-1} \rightleftharpoons H^+ + HPO_4^{-2}$$

Blood plasma is buffered in part by the bicarbonate system, consisting of carbonic acid (H_2CO_3) as a proton donor and bicarbonate (HCO_3^-) as a proton acceptor.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-.$$

<u>Methods expressing concentration of solution and calculation of volumetric analysis</u>

The different concentration indicated by different method:

1. **Formality:**

Is defined as the number of gram - formula weights of solute per liter of solution

$$F = \frac{Wt}{F.W} \times \frac{1000}{V\ ml}$$

Wt = Weight

F.W = Formula Weight

2. **Morality:**

Is defined as the number of moles (gram - molecular weight) of solute per liter of solution

$$M = \frac{Wt}{M.Wt} \times \frac{1000}{V\ ml}$$

Wt = Weight

M. Wt = Molecular Weight

3. **Normality:**

Is defined as the number of gram - equivalent weights of solute per liter of solution

$$N = \frac{Wt}{Eq.Wt} \times \frac{1000}{V\ ml}$$

Eq. Wt = Equivalent weight

Eq. Wt = Atomic weight / Oxidation number

4. **Percent concentration:**

Chemists frequently express concentrations in terms of percent (Part per hundred).

The concentration of a weight percentage composition solution is the number of grams of solute per 100 grams of solution three common methods are

$$Weight\ percent\ \left(\frac{W}{W}\right) = \frac{Wt\ of\ solute}{Wt\ of\ soln} \times 100$$

$$Volume\ percent\ \left(\frac{V}{V}\right) = \frac{Volume\ of\ solute}{Volume\ of\ soln} \times 100$$

$$Weight/Volume\ percent\ \left(\frac{W}{V}\right) = \frac{Wt\ of\ solute\ (g)}{Volume\ soln, ml} \times 100$$

5. **Molality:**

It is the number of moles of solute per 1000 grams of solven

$$Molality = \frac{No. of\ moles\ of\ solute}{1000\ g\ of\ olvent}$$

6. **Parts per million (ppm) and parts per billion (ppb):-** are used for extremely small concentrations

$$ppm = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

$$ppb = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^9$$

Preparation of standard solution

If a reagent is available in the pure state, a solution of definite normality is prepared simply by weighing out an equivalent weight, dissolving it in the solvent, usually water, and making up the solution to a known volume when the reagent is not available in the pure from as in the cases of most alkali hydroxides some inorganic acids, solution of the approximate normality required are first prepared.

These are then standardized by titration against a solution of a pure substance of known normality this indirect method is employed for the preparation of solution of most acid.

1- The gram - equivalent weight of an acid:

The weight of theacid which will furnish 1.008 gram of hydrogen as hydrogen ion H+

$$g.eq.wt\ of\ an\ acid = \frac{Gram - formula\ weight}{No.of\ H+}$$

2- The gram -equivalent weight of a base:

It is that weight of base in grams containing one gram equivalent of the hydroxyl radical OH

$$g.eq.wt\ of\ a\ base = \frac{Gram - formula\ weight}{No.of\ OH-}$$

3- The gram - equivalent weight of salt:

It is that weight of salt which contains one gram equivalent weigh of the contain or an ion. This quantity will be molecular weight of the salt divided by the total valence of the cation or anion.

4- The gram - equivalent weight of an oxidant or reductant (redox):

It is molecular weight divided by the number of electrons which (1) mole of the substance gains or losses in the reaction.

$$\text{g. eq. wt of reductant or oxidizing agent} = \frac{\text{Gram} - \text{formula weight}}{\text{N0. of electron gained or lost per molecule}}$$

<u>Calculation of Molarity or Normality from the labels bottle</u>

Usually the write very important information on the label of the bottle which contains the reagent such as:

- Density or specific gravity (Sp.gr)

- Concentration in percent %

From the above date we can calculate the normality or molarity of the reagent inside the bottle by using the following:

$$M = \frac{1000 \times specific\ gravity\ \times percentage\ ratio\ \%}{M.wt}$$

$$N = \frac{1000 \times specific\ gravity\ \times percentage\ ratio\ \%}{Eq.wt}$$

Dilution is one of the methods for preparing solutions of the desired normality. If N1 and V1 are the original normality and volume respectively, N2 and V2 are the normality and volume of the same solution of dilution then:

$$(N_1)(V_1) = (N_2)(V_2)$$

Equivalent weight in neutralization reactions :- The equivalent weight of acid is that weight of it which contains one-gramatom of replaceable hydrogen.

Eq.wt. acid = M. wt. of acid/ No.of active H^+

The equivalent weight of base is that weight of it which contains one replaceable hydroxyl group.

Eq. wt. base = M. wt. of base / No. of active OH^-

Examples:: Eq. wt of H_2SO_4=M. Wt. H_2SO_4 / 2

Eq. wt. of H_3PO_4= M.wt. of H_3PO_4 / 3

Eq. wt. of $Ca(OH)_2$=M. wt of $Ca(OH)_2$ / 2