

Syllabus

Water chemistry: Introduction, sources, and impurities in water, Potable water; meaning and specifications (as per WHO standards), Hardness of water, types, determination of hardness using EDTA titration, numerical problems on the hardness of the water. Biological oxygen demand (BOD) and Chemical Oxygen Demand (COD), Numerical problems on COD.

Methods of Chemical Analysis:

Volumetric Analysis: Introduction, principles of titrimetric analysis, the requirement of titrimetric analysis, the definition of equivalent weight, acidity, basicity, primary and secondary standards. Requirement of a primary standard solution, units of standard solutions (normality, molarity, molality, mole fraction, ppm).

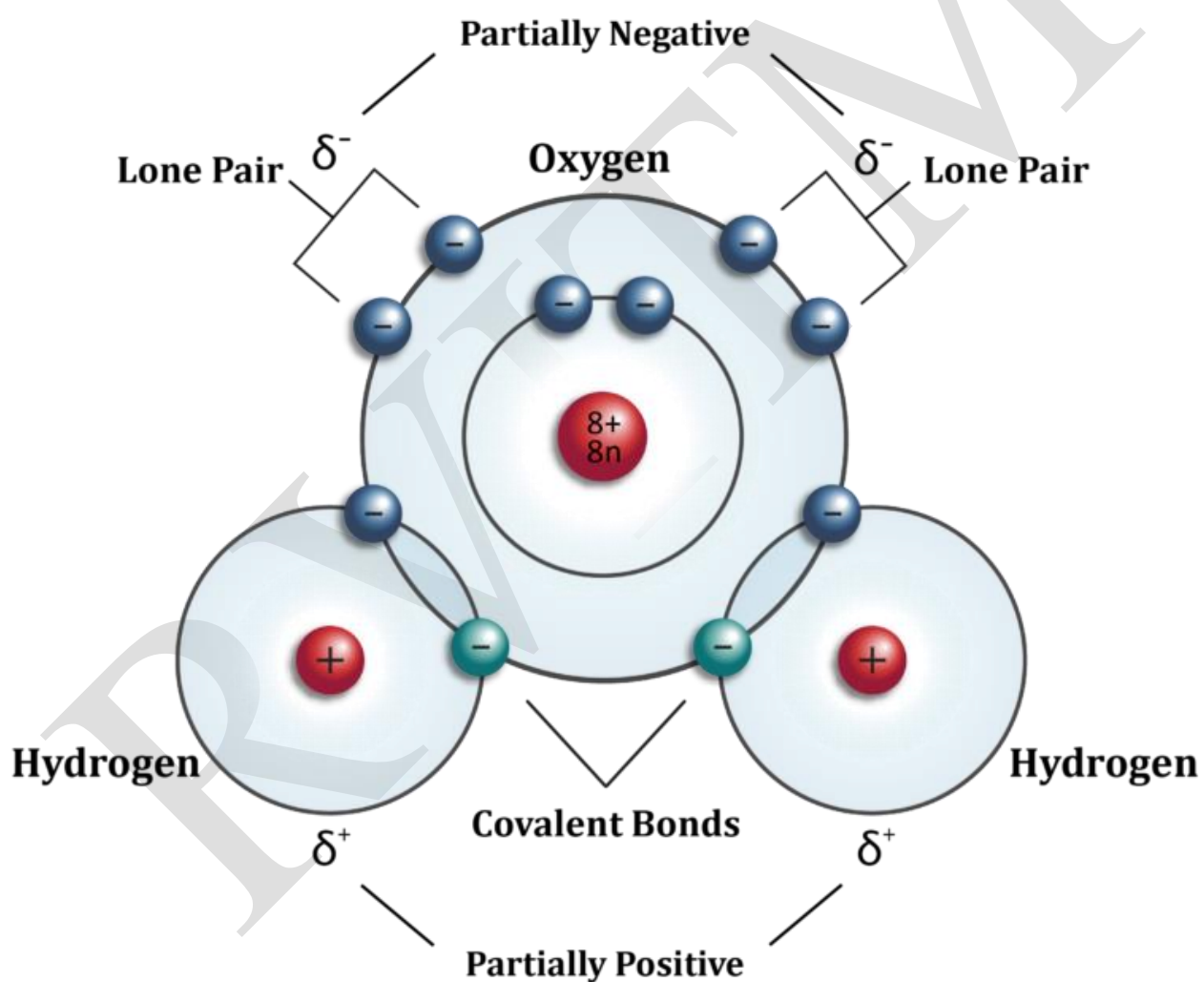
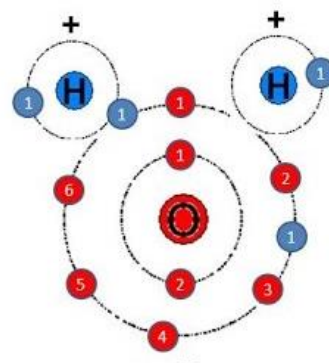
Instrumental methods of analysis: Introduction, Theory, Instrumentation, and applications of colorimetry, Flame Photometry, Atomic Absorption Spectroscopy, Potentiometry, Conductometry (Strong acid with a strong base, a weak acid with a strong base, a mixture of strong acid and a weak acid with a strong base).

Water Chemistry



Water

- Polar
- High specific heat
- Cohesion
- Adhesion



Introduction

Water is one of the most basic and essential components of all life. It covers nearly 72% of the earth's surface. It is the second most important substance required to sustain human, animal, and plant lives. Water is essential resource for living system, industrial processes, agricultural production, and domestic use.

Sources of Water

- i) Surface water and
- ii) Underground water

Surface Water

Surface water of four types, i.e.

- 1) **Rain water**: Rain water is supposed to be the purest form of water.
- 2) **River water**: River water contains dissolved minerals of soils such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium, and iron.
- 3) **Lake water**: Lake water has more or less a constant chemical composition, contains less of dissolved minerals.
- 4) **Sea water**: It is the most impure form of the water.

Underground Water

Spring and well water are from the underground water sources and in general clear in appearance due to the filtering action of soil.

Impurities in Water

The major categories of impurities found in the water may be broadly classified into four categories.

1. Dissolved impurities
2. Suspended impurities
3. Dissolved gases
4. Organic matter

Dissolved impurities

Dissolved impurities mainly consist of soluble salts of Ca, Mg, Na. I.e. bicarbonates, and chlorides, sulphates of Ca, Mg, and Na. In addition, small amount of nitrates, nitrites, silicates, ammonium and ferrous salts are also present. These salts are derived from the rock and soil with which the water is in contact. Thus, the water which is in contact with limestone contains CaCO_3 . Since the CO_2 dissolved in water interacts with limestone.



Similarly, water which is in contact with magnesite contains MgCO_3 .



In general ground water contains more dissolved salts than the surface water.

Suspended Impurities

Suspended matter may be inorganic or organic in nature. The inorganic materials include small particles of sand, clay, silica, hydroxides of iron and aluminium, derived from the erosion of soil. Some of these have large particle size and therefore settle down readily. Others are fine particles and colloidal in nature. These do not settle easily.

The organic suspended impurities are decaying vegetable matter and are due to microorganisms. These are also present in the colloidal form. This causes turbidity of water.

Dissolved Gases

Water contains mainly CO_2 and O_2 , SO_2 , NH_3 and oxides of nitrogen all of which are derived from atmosphere.

Organic Matter

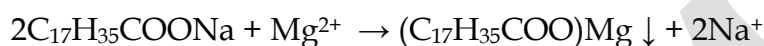
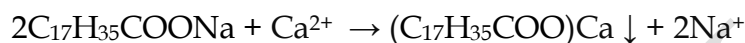
Organic impurities in water arise from the decay of vegetable matter. Mainly organic acids and from farming, paper making and domestic and industrial waste. These include detergents, fats, oils, solvents and residues from pesticides and herbicides. Water also contaminated with sewage and human excreta.

Potable water

Water that is fit for human consumption and free from pathogenic bacteria and toxic chemicals is called potable water.

Hardness of water

Hardness of water is due to the presence of soluble salts of calcium, magnesium and other heavier metals in water. Hard water does not give lather easily with soap, but produces a white scum or precipitate with soap. This is due to the formation of insoluble soaps of calcium and magnesium when the Ca and Mg ions react with soap. (Soaps are sodium and potassium salts of higher fatty acids such as oleic acid, palmitic acid and stearic acid).



There, soap can produce lather only after all the hardness causing ions are precipitated as insoluble soap. Hence, it requires large quantity of soap to produce lather. Thus, water which does not produce lather readily with soap is called hard water. On the other hand, water which produces lather easily with soap is called soft water.

Types of Hardness

- i. Temporary Hardness
- ii. Permanent Hardness

Temporary Hardness

Temporary hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium. This hardness can be removed by mere boiling of water, when bicarbonates are converted into insoluble carbonates.



Permanent Hardness

Permanent hardness is caused by the dissolved salts of calcium and magnesium, other than bicarbonates. They are chlorides, sulfates, nitrates, etc. Unlike temporary hardness, permanent hardness can not be removed by boiling. Removal of this hardness requires certain special chemical treatment methods.

The sum of temporary and permanent hardness is referred to as **total hardness of water**. The hardness is expressed in terms of equivalent calcium carbonate.

$$\text{Equivalence of CaCO}_3 = \frac{(\text{Mass of hardness causing salt}) \times (\text{Chemical equivalent of CaCO}_3)}{\text{Chemical equivalence of hardness producing salt}}$$

The units normally used to express hardness are **parts per million (ppm)** or milligrams per litre (mg/L) of calcium carbonate equivalents. Parts per million is the part of calcium carbonate equivalents per million (10^6) parts of water.

Determination of Hardness Using EDTA Titration

Hardness of water is mainly due to the presence of calcium and magnesium salts in it. Total hardness is the sum of temporary hardness (due to bicarbonates of calcium and magnesium) and permanent hardness (due to chlorides, sulphates etc., of calcium and magnesium). Ethylene diamine tetra acetic acid (EDTA) is a reagent, which reacts with metal ions like Ca^{2+} , Mg^{2+} forming complexes. Refer to Figure 5.1 for the molecular structure of EDTA. Therefore, this reagent can be used to determine the concentration of hardness causing substances. The amount of standard EDTA solution used during titration is a direct measure of the hardness.

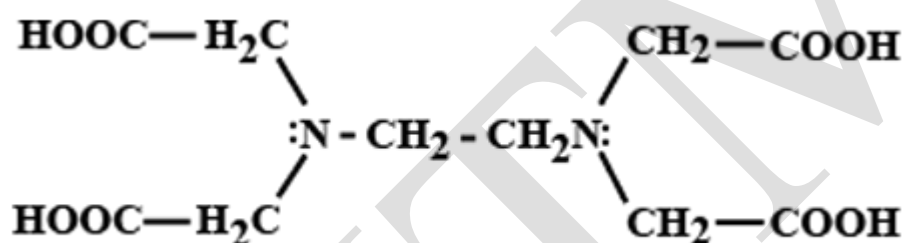
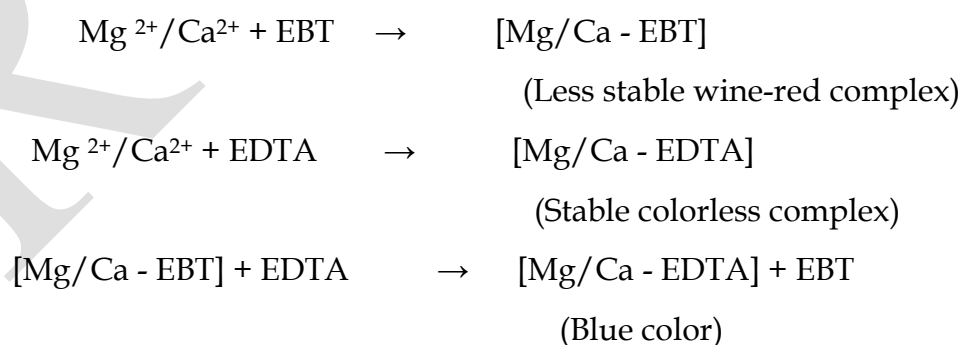


Figure. 5.1. Molecular structure of EDTA.

The completion of the reaction (end point of the titration) is identified using Eriochrome black-T indicator. It is a **blue colored organic dye**. It also forms relatively less stable complexes with bivalent metal ions of Ca^{2+} , Mg^{2+} etc., which are **wine-red** in color. Therefore, addition of the indicator to hard water produces wine-red color. When EDTA is added to hard water, it first reacts with free metal ions and then attacks the metal ion-indicator complex. The reaction can be represented as



So, at the end point a change from wine-red to blue color is observed. Since the reaction involves the liberation of H^+ ions and the indicator is sensitive to the concentration of H^+ ions (pH) of the solution, a pH of around 10 has to be maintained. For this purpose, ammonia – ammonium chloride buffer is used.

Procedure

Part-A: Preparation of standard EDTA solution

Weigh the weighing bottle containing disodium salt of EDTA (Fig. 1.2, dissolves fast and completely in water) accurately and transfer the salt onto the funnel placed on a 250 cm³ volumetric flask. Weigh the bottle again. The difference between the two weights will give the amount of EDTA transferred as shown in Table 1.1. Add about 2 cm³ of ammonia followed by water. Dissolve the salt by adding about 20-30 cm³ of de-ionized water. Make up the solution to the mark and shake well for uniform concentration.

Part-B: Estimation of hardness of water

Pipette out 25 cm³ of the given sample of hard water into a clean conical flask. Add 3 cm³ NH₃-NH₄Cl buffer followed by a pinch of Eriochrome black-T indicator. Titrate this against EDTA taken in a burette till the color changes from wine-red to pure blue. Note down the burette reading and repeat the titration to get concordant values.

Report: Total hardness of water = ppm.

Biological Oxygen Demand (BOD)

Biological Oxygen Demand is an important measure of water quality. **BOD is defined as the amount of oxygen required by microorganism to oxidize the organic matter in a water sample over a period of 5 days under aerobic condition at 20 °C.**

Characteristics of BOD

- The unit of BOD is mg/dm³ or ppm.
- Determination is slow and time-consuming method.
- It represents only biodegradable organic matter under aerobic condition.

Determination of BOD by Winkler's Method

Principle

In this method BOD is determined by measuring the DO content before and after 5 days period by indirect iodometric method. The given sample of water is treated with manganese sulphate and alkaline KI solution. In alkaline medium, DO oxidize Mn²⁺ to Mn⁴⁺, which gets precipitated as MnO₂.H₂O. On acidification, Mn⁴⁺ reverts to Mn²⁺ which oxidizes potassium iodide to free iodine. The liberated iodine is then titrated with standard Na₂S₂O₃ using starch as indicator till the disappearance of blue colour.

Procedure

A known volume of sewage sample is diluted to definite volume with water which contains nutrients for bacterial growth and sufficient oxygen. Equal volumes of diluted sample are filled into 2 BOD bottles.

Blank titration

DO content in one of the BOD bottles is determined immediately.

3 ml MnSO_4 solution and 3 ml alkaline KI solution is added into the bottle shake well and allow the precipitate to settle down. 1 ml of concentrated H_2SO_4 is added slowly and mixed well until the precipitate dissolves completely. A known volume of this solution is titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ using freshly prepared starch as indicator till discharge of blue colour. Record the volume of the $\text{Na}_2\text{S}_2\text{O}_3$ solution used (D_1).

Sample titration

The second bottle is incubated for 5 days at 20°C . After 5 days unconsumed DO is measured as described above. (D_2). Then BOD is calculated from the formula

$$BOD = \frac{D_1 - D_2}{A} \times B \text{ mg/dm}^3$$

Where D_1 is the DO in the solution at start, D_2 is the DO in the solution after 5 days, 'A' is the volume of the sample before dilution and 'B' is the volume of the sample after dilution.

Chemical Oxygen Demand (COD)

It is defined as the **amount of oxygen required for the complete oxidation of both organic & inorganic matter present in 1 litre of waste water using strong oxidizing agent like potassium dichromate in acidic medium.**

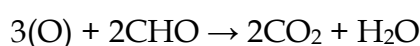
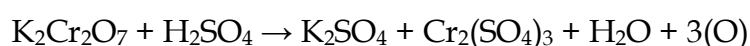
Characteristics of COD

- The unit of COD is mg/dm^3 or ppm.
- In general $\text{COD} > \text{BOD}$ since both biodegradable and non-biodegradable organic load are completely oxidized.

Determination of COD of Waste Water

Principle

In this method, the given samples of water containing organic and inorganic impurities are oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic media in the presence of catalyst Ag_2SO_4 and HgSO_4 . (Added to prevent the interference the chloride and silver ions). The unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ is titrated against FAS solution in the presence of a redox indicator, ferroin which shows its colour change in the oxidized (bluish green) and reduced states (reddish brown).



Procedure

Preparation of standard solution and Determination of COD

Standard FAS solution is prepared by adding dilute H_2SO_4 (Added to prevent hydrolysis of FAS) to a known weight of FAS salt.

1. Pipette out known amount of the waste water into a clean conical flask.
2. Add 10 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ and 10 ml 1:1 H_2SO_4 into a conical flask.
3. Add 1 g of Ag_2SO_4 followed by 1 g of HgSO_4 and warm if necessary.
4. Titrate with standard FAS using ferroin as indicator till colour changes from bluish green to reddish brown.
5. Note down the volume of FAS consumed as ' V_1 ' ml.
6. Perform the blank titration without waste water sample. Note down the volume as ' V_2 ' ml.

Calculations:

Normality of FAS = "N"

Volume of the waste water = "V" ml

Volume of FAS consumed in back titration = " V_1 " ml

Volume of the FAS consumed in blank titration = " V_2 " ml

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ in terms of FAS = $(V_2 - V_1)$ ml

1000 ml of 1 N FAS = 8 g of O_2

1 ml of 1 N FAS = 0.008 g of O_2 = 8 mg of O_2

V_1 ml of 1 N FAS = $0.008 \times V_1 \times N$ g of O_2

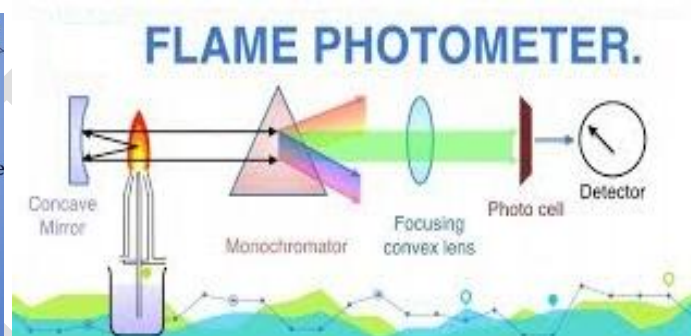
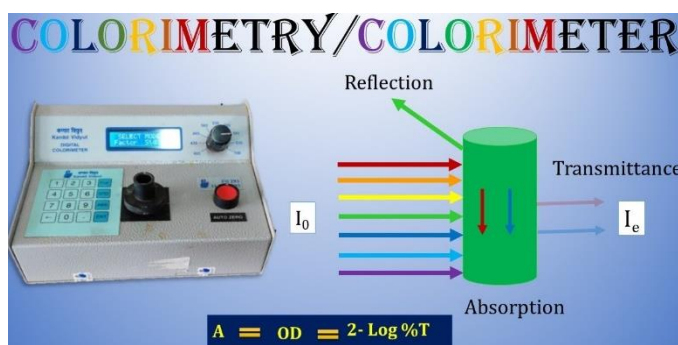
V ml of water sample contains = $0.008 \times V_1 \times N$ g of O_2

1000 ml of water sample contains = $\frac{N \times V_1 \times 8 \times 1000}{V}$ mg/l of O_2

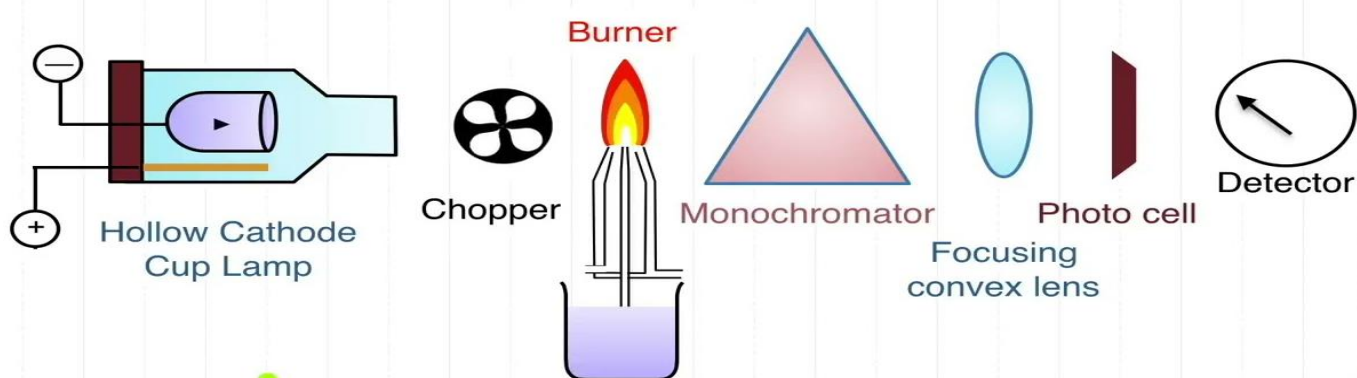
For blank titration = $\frac{N \times V_2 \times 8 \times 1000}{V}$ mg/l of O_2

Therefore COD of waste water = $\frac{N \times (V_2 - V_1) \times 8 \times 1000}{V}$ mg/l of O_2

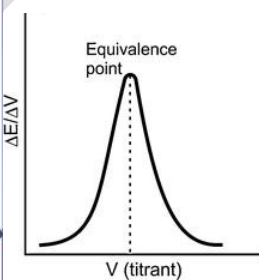
Methods of Chemical Analysis



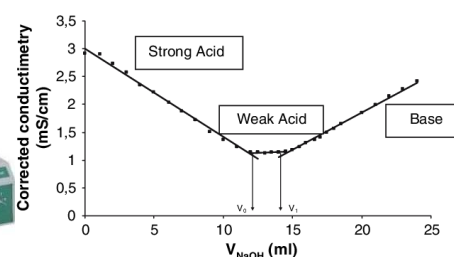
ATOMIC ABSORPTION SPECTROMETER.



Potentiometry



CONDUCTOMETER



Analytical chemistry → Branch of chemistry that deals with chemical analysis

Chemical analysis → Involves identifying and determining the percentage composition in a sample of a substance. Identification is carried out by qualitative analysis. Quantitative analysis gives the percentage composition of the constituents

Important techniques of quantitative analysis

- Titrimetric or Volumetric
- Gravimetry
- Instrumental methods

Volumetric Analysis

Volumetric analysis is a quantitative analytical method. As the name suggests, this method involves measurement of the volume of a solution whose concentration is known and applied to determine the concentration of the analyte.

In other words, measuring the volume of a second substance that combines with the first in known proportions is known as Volumetric analysis or titration. It is this method of quantitative analysis that allows us to determine the concentration of the analyte. The first method of Volumetric Analysis was devised and found by the French chemist Jean-Baptiste-Andre-Dumas; as he was trying to determine the proportion of nitrogen combined with other elements in organic compounds. To ensure the conversion of the nitrogen compound into pure gas, the nitrogen compound was burnt in a furnace and passed along a furnace in a stream of carbon dioxide that is passed into a strong alkali solution. The mass of the nitrogen is calculated and occupies under known conditions of pressure and volume from the sample

principles of titrimetric analysis

1. The solution to be analysed contains an unknown amount of chemicals.
2. The reagent of unknown concentration reacts with a chemical of an unknown amount in the presence of an indicator (mostly phenolphthalein) to show the end-point. It's the point indicating the completion of the reaction.
3. The volumes are measured by titration which completes the reaction between the solution and reagent.
4. The volume and concentration of reagent which are used in the titration show the amount of reagent and solution.
5. The amount of unknown chemical in the specific volume of solution is determined by the mole fraction of the equation.

When the endpoint of the reaction is reached, the volume of reactant consumed is measured and applied to carry volumetric analysis calculations of the analyte by the following formula,

$$C_a = C_t V_t M / V_a$$

Where,

C_a is the analyte concentration, typically in molarity.

C_t is the titrant concentration, typically in molarity.

V is the volume of the titrant which is used, typically in liters.

M is the mole ratio of the analyte and reactant from the balanced equation.

V is the volume of the analyte, typically in liters.

Many non-acid-base titrations are needed a constant pH throughout the reaction. Therefore, a buffer solution can be added to the titration chamber to maintain the pH value.

Equivalent weight

The number of parts by weight of the substance which combines with or displaces 1 part by weight of hydrogen, 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

Equivalent weight of an acid: The ratio of molecular weight of acid to basicity of acid or the ratio of molecular weight of acid to the number of hydrogen atoms replaced in one molecule of acid during the reaction.

Equivalent weight of a base: The ratio of molecular weight of base to acidity of acid or the ratio of molecular weight of base to the number of OH^- groups replaced in one molecule of base during the reaction.

Equivalent weight of an oxidizing agent or reducing agent: The ratio of molecular weight of the substance to the number of electrons gained or lost by one molecule during a redox reaction.

Acidity

Acidity is the extent which a substance will donate a proton/hydrogen ion. Substance with high acidity will donate a proton easily while substance with low acidity will rarely donate protons and in presence of more acidic substance, accept a proton.

Basicity

Basicity is the extent to which a substance will accept a proton/hydrogen ion.

Standard solution

The solution whose concentration is known accurately.

Primary standard solution

A substance which is available in highly pure state, neither hygroscopic nor efflorescent and is stable under the conditions of storage is called primary standard substance. A solution prepared using a primary standard is called primary standard solution.

Example: $K_2Cr_2O_7$, oxalic acid, $AgNO_3$, KCl , anhydrous sodium carbonate, PHP, etc.

Secondary standard solution

A substance which is not available in highly pure state, is hygroscopic or efflorescent and is not stable under the conditions of storage is called secondary standard substance. A solution prepared using a secondary standard is called secondary standard solution.

During the preparation of secondary standard solution an approximate weight of such a substance is dissolved in water and then the strength of this solution is determined by titrating against a primary standard solution this is known as standardization.

Example: $NaOH$, $KMnO_4$, HCl etc.

Requirement of a primary standard solution

Units of standard solutions

Normality (N)

The number of gram equivalent weight of a substance dissolved in $1dm^3$ of solution.

Mass of the substance (in $1 dm^3$) = Normality \times gram equivalent weight of the substance

Molarity (M)

The number of moles of solute present in $1dm^3$ of solution.

Mass of the substance (in $1 dm^3$) = Molarity \times gram equivalent weight of the substance

Molality

Number of moles of solute present in 1 kg of a solvent.

Mole fraction

Mole fraction represents the number of molecules of a particular component in a mixture divided by the total number of moles in the given mixture.

Parts per million (ppm)

It denotes amount of a substance per 1,000,000 or 10^6 parts of solution regardless of the units of measure used as long as they are same.

Instrumental methods of analysis

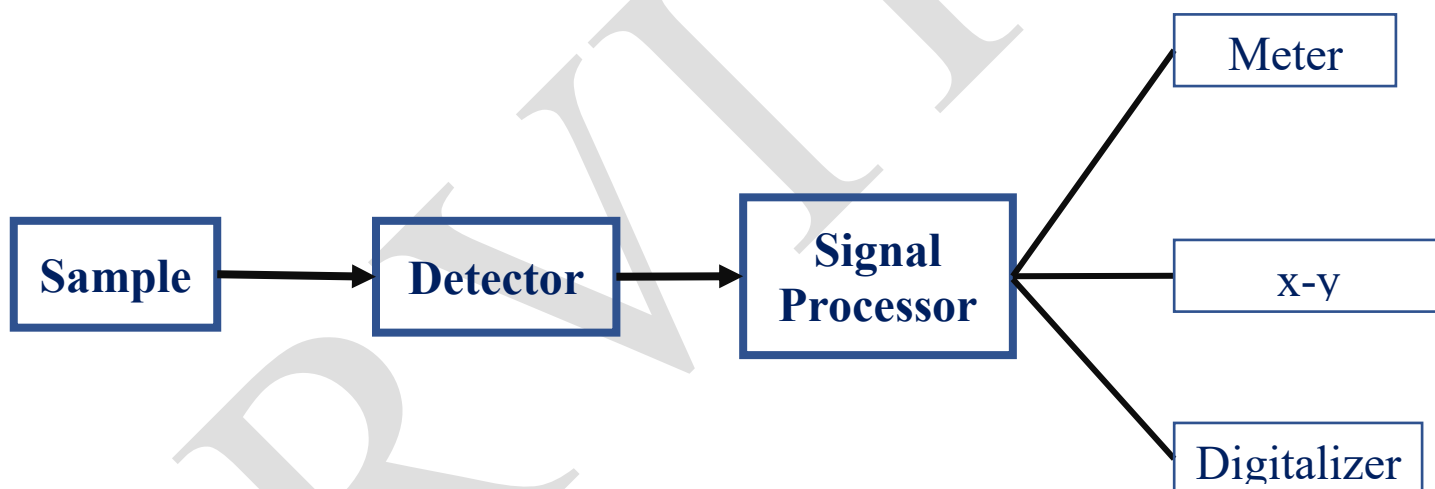
- Methods based on emission or absorption of radiation
- Electrochemical methods such as potentiometry, conductometry and polarography
- Mass spectrometry
- Methods based on measurements

Theory

In instrumental methods of analysis, the analytical instrument converts an analytical signal from the analyte into an electrical signal that can be measured by suitable device. The electrical signal that can be read on a meter is a measure of the quantity of the sample.

Eg.

- A photometer measures the amount of light absorbed by a colored solution (analytical signal) by converting the light radiation into an electrical signal. The later is measured by a galvanometer
- A pH meter measures the electrical potential developed at an electrode interface due to hydrogen ion concentration (analytical signal)



Block diagram of an analytical instrument

Advantages

- They require small quantities (less than a milligram) of the analyte
- Methods adopted are easy when a large number of analytes have to be analyzed
- The analysis can be conducted in a very short time
- They give accurate results

Limitations

- The instruments are expensive
- An initial or continuous calibration is required using a sample of materials of known composition
- The concentration range is limited
- Specialized training is needed for the operation of certain sophisticated instruments

Colorimetry

Theory of Colorimetry

When a beam of light falls upon a homogeneous medium, a fraction of the incident light (photons) is reflected, absorbed within the medium, and remaining is transmitted. The fraction of light absorbed depends on

- a) Nature of the absorbing species
- b) The concentration of the absorbing molecules and
- c) The path length (i.e., the distance covered by the light in the solution).

Principle

When a monochromatic light of intensity I_0 is incident on a transparent medium, a part I_a of it is absorbed, a part I_r of it is reflected and the remaining part I_t is transmitted. This is given as

$$I_0 = I_a + I_r + I_t$$

For a glass air interface I_r is negligible, therefore $I_0 = I_a + I_t$

$I_t / I_0 = T$ is called the transmittance, $\log 1 / T = \log I_0 / I_t$ is called the absorbance or optical density.

The relation between absorbance A , concentration c (expressed in mol / dm^3) and path length t

(expressed in cm) is given by Beer - Lambert's law, $A = \log I_0 / I_t = \epsilon bc$

where ϵ is the molar extinction co-efficient, B is the path length & C is concentration and A is absorbance of a substance at a given wavelength.

If t , the path length is kept constant, then $A = \epsilon bC$. Hence a plot of absorbance against concentration gives a straight line.

The Beer-Lambert law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

$$A = \epsilon bC$$

Instrumentation

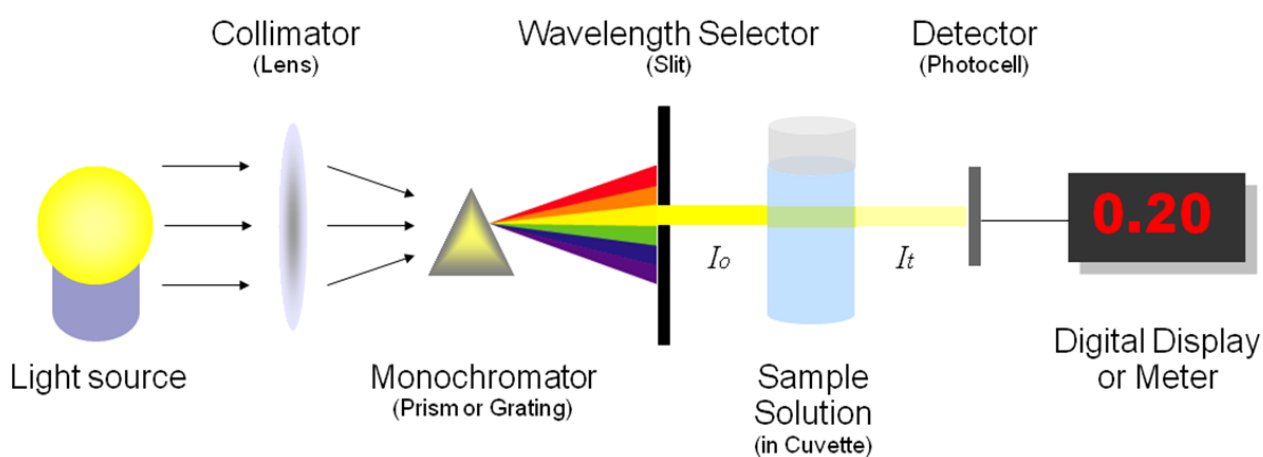


Figure 5.2. Colorimetry

Basic modern colorimeters consist of (Figure 5.2)

- a) Source of light:** Tungsten filament lamp is used between the wavelength range 400-760 nm. For UV and IR region hydrogen discharge lamp and Nernst Glower is respectively used.
- b) Monochromator:** It should provide narrower wavelength bands. Glass prism/ grating is used in visible region whereas quartz and alkali halide prisms are respectively used in UV and IR region.
- c) Sample holder:** The sample holder is to hold the sample solution for analysis. Fused glass cells are used in the wavelength range of 300-2500nm. Corex glass or quartz cells are used in the wavelength range 210-300 nm and fused silica cells are used in much lower wavelengths.
- d) Photo diode:** It is used to convert the light transmitted and into an electrical signal. A phototube or photodiode is used as a photovoltaic cell.
- e) Meter:** It is to read the electric signal directly as absorbance or transmittance.

Working of Colorimeter:

- Transfer the given copper sulphate solution (stock solution) to a burette and draw out 5,10,15,20 and 25cm³ of solution into 50 cm³ volumetric flasks.
- Add 5cm³ of ammonia solution (*using 50 cm³ burette, don't use pipette*) to each of them and dilute upto the mark with ion exchange water.
- Stopper the flasks and mix the solution well.
- To the test solution given in a 50 cm³ measuring flask, add 2 cm³ of ammonia solution, then dilute upto the mark with ion exchange water and mix well.
- Prepare a blank solution by diluting 5 cm³ of ammonia solution in 50 cm³ volumetric flask and dilute up to the mark with ion exchange water and mixing well.
- After 10 minutes, measure the absorbance of the solutions against blank at 620nm using a photo electric colorimeter.

Tabulate the readings, plot a calibration curve (Figure 5.3), as shown below

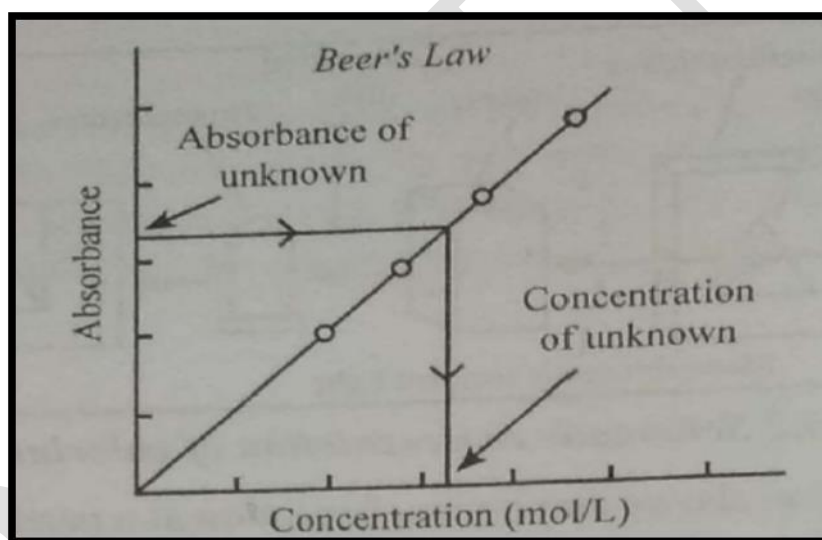


Figure 5.3. Calibration curve

Find out the concentration of copper solution given i.e. the volume of test solution and calculate the amount of copper in the given test solution.

LIMITATIONS OF COLORIMETRY

- Deviations in absorptivity coefficients at **high concentrations** ($>0.01M$) due to electrostatic interactions between molecules in close proximity
- **scattering of light due to particulates** in the sample
- **Fluorescence or Phosphorescence** of the sample
- Changes in refractive index at high analyte concentration

- Shifts in chemical equilibria as a function of concentration
- Non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band stray light

Flame Photometry

Principle

Flame photometry is an atomic emission technique used for detection of alkali metals. It works on the basis that if a solution containing metallic salts is aspirated into a flame, a vapour, which contains metallic atoms, will be formed. These metallic atoms are then excited from ground state (E_1) to higher energy state E_n where $n=2,3,4,7$, by making use of thermal energy of flame. From higher energy states these atoms will return to the ground state by emitting radiations ($E_n - E_1 = h\nu$ where $n=2,3,4,\dots,7$), which are the characteristic of each element.

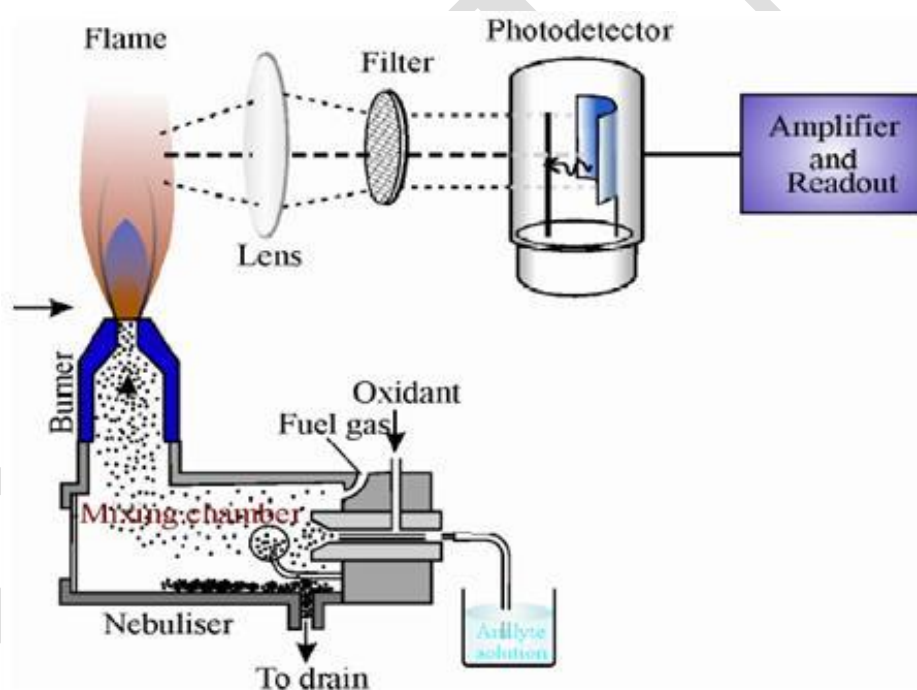


Figure 5.4. Flame photometry

Flame photometer correlates the emitted radiations with the concentration of these elements. It is simple and rapid method for the elements that can be easily excited (Sodium and other alkali metals)

A flame photometer is composed of the pressure regulator and flow meter for fuel gases an automizer, burner, optical system, photosensitive detector and output recorder (Figure 5.4). A filter of the element whose concentration is to be determined is inserted between the flame and the detector. Propane gas is used as fuel and air or oxygen is used as oxidant.

Combination of these two will give a temperature of 1900°C , which is required for the experiment. The whole analysis depends on the flow rate of the fuel oxidant, the rate of introduction of the sample and droplet size.

The sample containing the analyte is aspirated into the flame through atomizer. Radiation from resulting flame is collected by the lens and allowed to pass through an optical filter, which permits only the radiation characteristic of the element under investigation to pass through the filter and photocell. The output from the photocell is displayed digitally on the flame photometer.

Estimation of Na and K in a given water sample.

Standard solution of sodium and potassium of concentrations 2, 4, 6, 8 & 10 ppm are prepared from stock solution of 50 ppm into different 50 cm³ Volumetric flasks. The solutions including the solution of unknown concentration were diluted up to the mark using distilled water and shaken well for uniform concentration. Flame photometer readings of all the solutions were recorded using a flame photometer. Concentrations of Na⁺ and K⁺ in the unknown solution were determined by plotting a graph (Figure 5.5) of flame photometer readings against concentration of sodium & potassium solution.

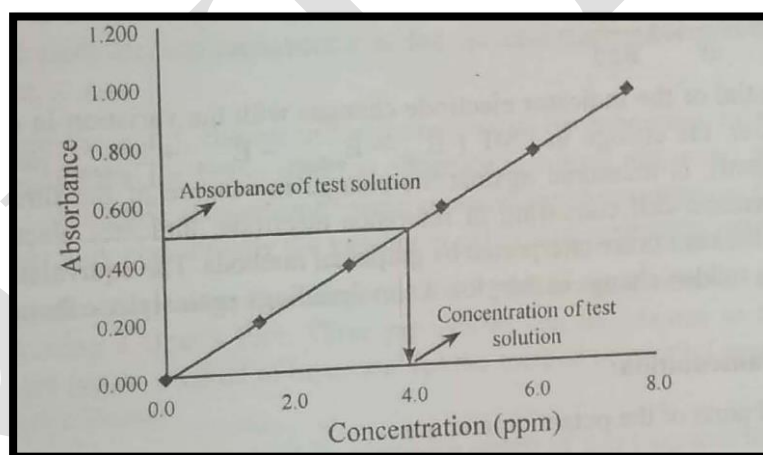


Figure 5.5. Calibration curve

Flame photometry limitations

Unlike other spectroscopy methods flame photometry find limited application in research and analysis. This is due to,

- A limited number of elements that can be analyzed.
- The sample needs to be injected as fine droplets into the flame. Several metallic salt, soil, plant and other compounds are insoluble in common solvent. Hence, they can't be injected directly.

- Since the sample is Volatilized, if a small amount of sample is present it is difficult to analyze by this method because some of it is wasted by Vaporization.

Potentiometry

It is an electro analytical technique in chemical analysis. Potentiometer measurement system consists of (Figure 5.7)

- Two electrodes called reference and indicator electrode
- Potentiometer
- A solution of the analyte and oxidizing agent.

Principle

Nernst equation gives the relation between potential of the electrode and the concentration of the active species in the solution.

The Nernst equation is given as

$$E = E^0 + \log [\text{Oxidized form}] / [\text{Reduced form}]$$

Where E^0 is the standard electrode potential and the terms in the brackets are concentrations. It can be easily understood by the equation that potential depends on the concentrations of oxidized and reduced species in the solution.

When a reducing agent in solution is oxidized using an oxidizing agent the concentrations and potential changes. Potentiometry is the measurement of change in potential when a solution is oxidized or reduced. When a reducing agent is titrated against an oxidizing agent in presence of electrodes like platinum and calomel are connected to potentiometer potential increases gradually and increases rapidly at the end point. When a graph of change in potential against volume of oxidizing agent is plotted the sudden change in potential will be the equivalence point. The sudden change can be explained as that the potential increase in the beginning due to slow oxidation of ferrous iron to ferric iron and the equation given below holds good.

$$E = E^0 + 2.303 \frac{RT}{nF} \log \frac{[\text{ox}]}{[\text{Red}]}$$

Thus, the potential depends on the concentrations of ferric and ferrous ions. Near the end point concentration of ferrous ions becomes very small, and the ratio of $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$ increases rapidly. Thus, the emf increases rapidly close to the end point. Beyond the

equivalence point no ferrous ion exists, and the potential depends on dichromate and chromium ions.

Thus, after the end point, it is the electrode potential of the $\text{Pt}/[\text{Cr}^{6+}]/[\text{Cr}^{3+}]$ electrode, which is going to change. Because of both factors, there is a large change in potential at the end point.

Plot a graph of $\Delta E/\Delta V$ volume of dichromate solution added and find out the equivalence point (Figure 5.8). Calculate the normality of ferrous ammonium sulphate solution and the amount of iron in the given volume of the solution.

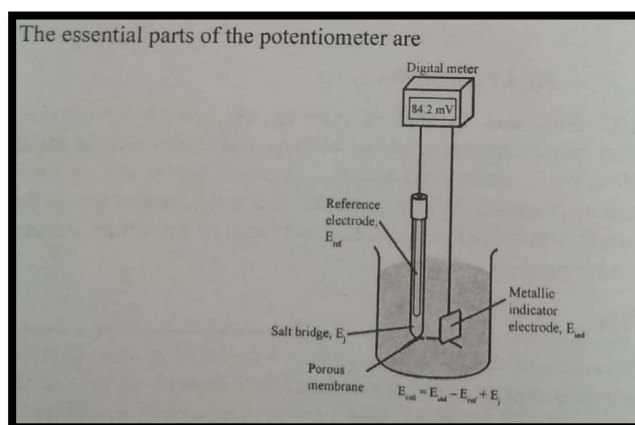


Figure 5.7. Electrochemical cell for the potentiometric titration.

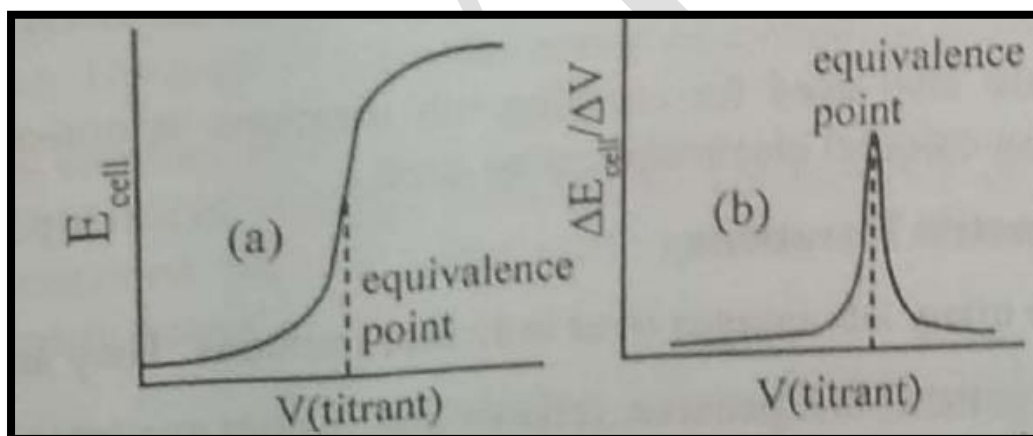


Figure 5.8. Volume vs voltage & $\Delta E/\Delta V$ plot for a potentiometric titration.

Applications

- To determine the pH of a given solution employing glass/calomel electrode.
- Complexometric titrations can be followed with an electrode of the metal whose ion is involved in complexometric titrations. e.g. A silver electrode may be used to follow the titration of cyanide ion with a standard solution of Silver.

- It is used in redox titrations using an inert electrode. e.g. Monitoring of Cyanide wastes from metal plating industries or chlorine compounds in bleach compounds manufacturing, and use of these bleach compounds in paper manufacturing. They are also extensively used in water pollution, sewage treatment, agricultural and biochemical studies.
- They are used in precipitation titrations that involves insoluble salts of metals like silver, mercury, lead, and copper. e.g. Determination of chloride ion with a standard solution of silver nitrate using silver metal indicator electrode and SHE as a reference electrode.
- Potentiometric titrations are also used for carrying out titrations in non-aqueous solvents.

Advantages of Potentiometric Titrations

- The apparatus required in general inexpensive, reliable and readily available.
- It is easy to interpret titrations curves
- It can be used for colored solutions.
- No Indicator is required for this analysis.

Conductometry

The principle of measurement of conductivity includes the use of a conductivity cell (consisting of two platinum electrodes) placed in the analyte (sample) solution, and a potential is applied across them. The conduction of electricity in a sample solution is because of the migration of cations and anions towards the respective cathode and anode.

Though the movement of the ions occurs in the solution, it remains electrically neutral throughout. The mobility of an ion takes place under the influence of an applied voltage or a concentration gradient. It is affected by various factors such as the charge, size, mass, and extent of solvation.

Conductivity (C), the inverse of the resistivity(R), is determined from the voltage and current values(I) according to Ohm's law

$$C = \frac{1}{R}$$

It is expressed in terms of Siemens(S) or mho. Specific conductivity(K) simply is the measure of conductance by placing a cell having a unit area of a cross section of the electrode and placed at a unit distance apart. This expressed as

$$K = C \frac{L}{A} \mu S/cm$$

Instrumentation

- Conductivity cell- it is constructed by a Pyrex or other resistance glass fitted with

a pair of Pt or platinized electrodes (Figure 5.9)

- Conductivity meter- to display the reading during titration.
- Thermostat- to maintain the constant temperature.
- Magnetic stirrer- the conductivity cell is dipped in the analyte solution and placed on the magnetic stirrer to maintain the uniform concentration after each addition.

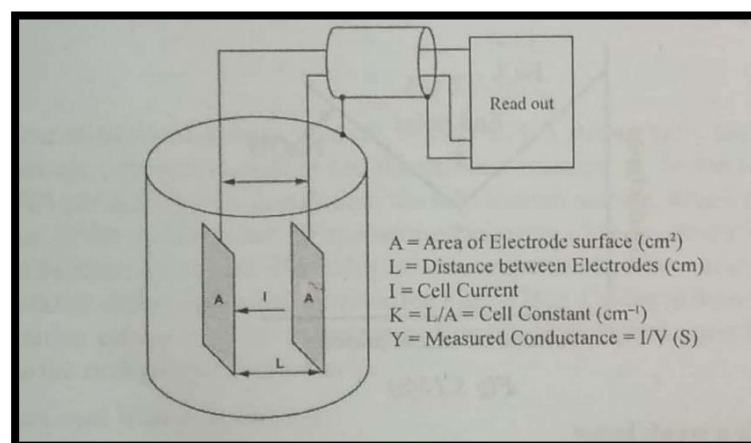


Figure 5.9. Instrumentation for conductometric titration

Experimental

A simple arrangement for the measurement of conductance is shown in the above diagram, the analyte solution whose conductance is to be estimated is taken in a beaker. The conductivity cell is dipped in the solution and mixed with using magnetic stirrer and, a constant temperature is maintained with the help of a thermostat. Further, it is connected to the conductivity meter and initial conductance is measured. The titrating reagent is added in small proportions, and conductance of the solution is measured after stirring. The addition of the titrating reagent is continued until at least five readings beyond the equivalence point. A graph is prepared by plotting the conductance readings against the volume of the titrating reagent. The two straight portions of the curve are extrapolated until they intersect and the point of intersection is taken as the equivalence point of the titration.

Conduct metric titration curves

Strong acid with a strong base

Let us consider the reaction between HCl and NaOH



At the start of the titration, the acid solution has high conductivity due to highly mobile H^+ ($350\mu\text{Scm}^{-1}$) ions. The conductivity due to Cl^- is less because of their lower mobility as compared with H^+ ions. When NaOH is added, the more mobile H^+ ions are replaced by less mobile Na^+ ($40\text{--}80\mu\text{Scm}^{-1}$) ions, this will result in the rapid decrease of conductivity.

The solution at the end point (neutralization point) containing only Na^+ and Cl^- ions and hence it has minimum conductivity. Now, if NaOH is added, the conductivity will rise due to the increase of OH^- ($198 \mu\text{Scm}^{-1}$) ions, because these ions have more mobility than Na^+ ions. Therefore, the titration carried out at constant temperature and the conductivity is plotted versus the volume of NaOH added (Figure 5.10), the point of crossing of two lines gives the Equivalence point.

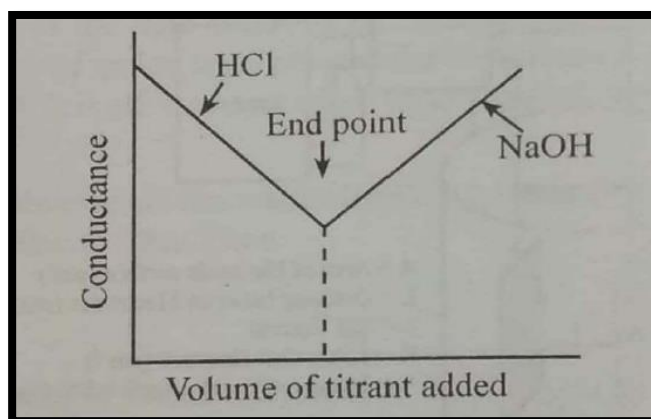


Figure 5.10. Volume vs conductance plot for the conductometric titration of strong acid with a strong base.

Strong acid with a weak base



The titration of a strong acid (HCl) with a weak base (NH_3 Solution) is shown in the below diagram (Figure 5.11). The first line of the graph reveals the disappearance of the hydrogen ions during the neutralization due to the replacement of more mobile H^+ ions with less mobile NH_4^+ ions, but after reaching the end point the graph becomes almost horizontal. This is because of the addition of ammonia after the endpoint is weakly ionized in the presence of ammonium chloride and therefore its conductivity is small.

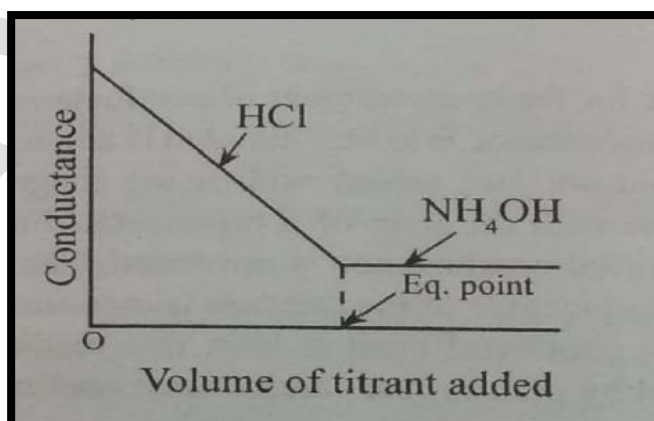


Figure 5.11. Volume vs conductance plot for the conductometric titration of strong acid with a weak base.

Weak acid with a strong base



In the titration of a weak acid with a strong base, the shape of the curve (Figure 5.12) depends upon the concentration and dissociation constant K_a . In the titration of the acetic acid with sodium hydroxide solution, the salt, sodium acetate, which is formed during the first part of the titration tends to oppose the ionization of acetic acid still present and hence the conductance decreases. The rising salt concentration will, however, tend to increase the conductance of the solution as shown in the diagram below. Owing to these opposing influences the titration curves may have minima and its position depend upon the concentration as well as the strength of the weak acid.

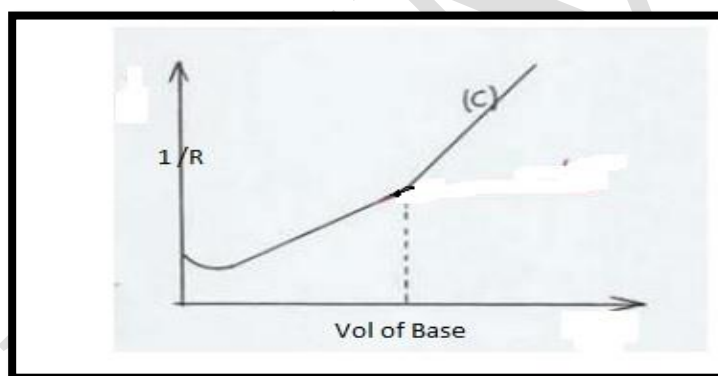
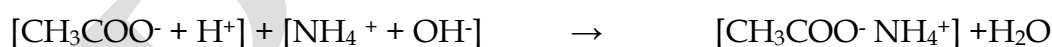


Figure 5.12. Volume vs conductance plot for the conductometric titration of weak acid with a strong base.

Weak acid with a weak base



In the titration of weak acid with a strong base, the shape of the curve depends upon the concentration and dissociation constant K_a . In the titration of the acetic acid with sodium hydroxide solution, the salt, sodium acetate, which is formed during the first part of the titration tends to oppose the ionization of acetic acid still present and hence the conductance decreases (Figure 5.13). The rising salt concentration will, however, tend to increase the conductance of the solution as shown in the diagram below. Owing to these opposing influences the titration curves may have minima and its position depend upon the concentration as well as the strength of the weak acid.

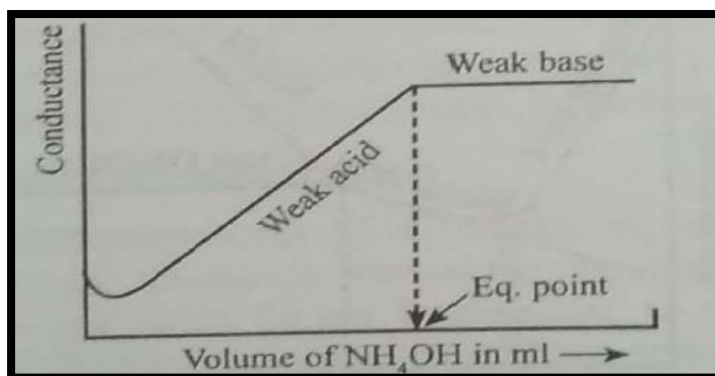


Figure 5.13. Volume vs conductance plot for the conductometric titration of weak acid with a weak base.

Mixture of Strong acid and a weak acid with a strong base

Upon adding a strong base (NaOH) to a mixture of a strong acid (HCl) and a weak acid (CH_3COOH), the conductance falls until strong acid is neutralized, then rises as the weak acid is converted into its salt (CH_3COONa), and finally more steeply as excess alkali is added and it is exhibited as shown in the diagram below (Figure 5.14). All three lines are straight and their intersections correspond to the endpoints of the individual acids.

The addition of a weak base, like ammonia solution to the acid mixture has little effect upon the conductance after the equivalence points due to suppressing the ionization of ammonia by ammonium acetate salt present in the solution.

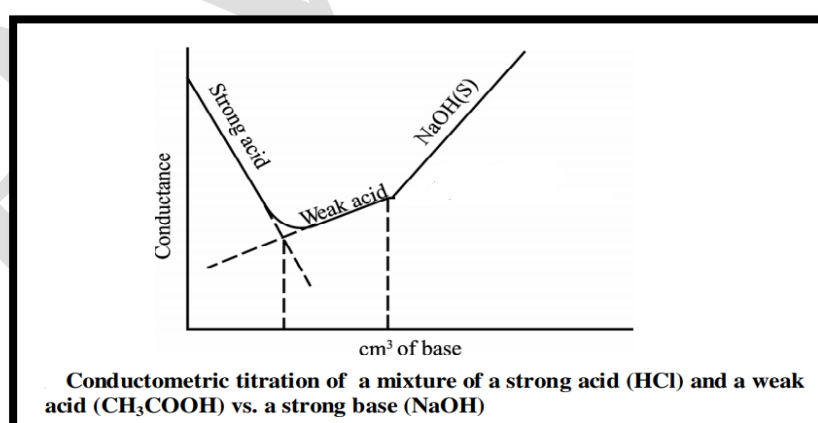


Figure 5.14. Volume vs conductance plot for the conductometric titration of mixture of acids with a strong base.

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