MODULE 5: SENSORS IN ANALYTICAL TECHNIQUES

Electrode System: Introduction, types of electrodes. Ion selective electrode – definition, construction, working and applications of glass electrode. Determination of pH using glasselectrode. Reference electrode- Introduction, calomel electrode– construction, working and applications of calomelel ectrode. Concentration cell– Definition, construction and Numerical problems.
Sensors: Introduction, working principle and applications of Conductometric sensors, Electrochemical sensors, Thermometric sensors, and Optical sensors.
Analytical Techniques: Introduction, principle and instrumentation of Colorimetric sensors; its application in the estimation of copper, principle and instrumentation of Potentiometric sensors; principle, instrumentation and its application in the estimation of iron, Conductometric sensors; its application in the estimation of weak acid.

ELECTRODE SYSTEM

Types of electrodes:

1) ***Metal-metal ion exchange:*** In this electrode, a metal is immersed in the ionic solution of its own salts. Example: Cu/Cu^{2+}
2) ***Redox electrode:*** In this electrode, ions of a chemical species in two different oxidation states are in contact with each other. Example: Pt
3) ***Gas Electrode:*** In this electrode, an inert metal like platinum is in contact with gas molecules Examples: Standard Hydrogen electrode
4) ***Metal-Insoluble salt electrode:*** In this electrode, metal is in contact with its insoluble salt. Example: Calomel Electrode
5) ***Amalgum electrode:*** In this electrode, a known concentration of metal dissolved in liquid mercury is in contact with ionic solution of the metal. Example: Pb(Hg)
6) ***Ion selective electrode:*** This electrode is more selective towards a particular type of ion in the mixture. Example: Glass electrode

Ion-selective electrode

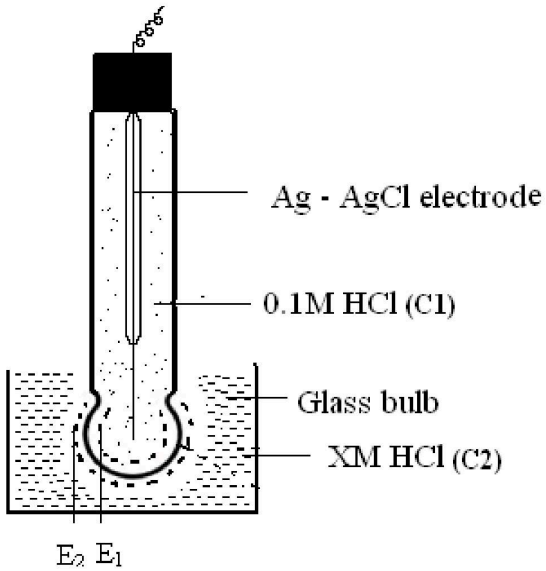
The electrode, which are responds to a specific ion in a mixture by ignoring other ions are called as ion selective electrodes. They consist of a thin membrane in contact with ion solution. Example, glasselectrode

Glass Electrode:

This electrode works on the principle that when a thin, low resistivity glass membrane is in contact with a solution containing H^+ions, a potential develops across the membrane and the solution. Potential developed depends on the concentration of hydrogen ions in thesolution.

Construction:

- It consists of a long glass tube with a thin-walled glass bulb containing 0.1 M HCl [C_1]. Ag/AgCl electrode placed inside the solution to provide electrical contact.
- The glass electrode is dipped in unknown solution of concentration C_2.
- Thepotential developed across the membraneby the exchange of ions with the composition of glass is known as the boundary potential E_b (E_2– E_1).
- Even when C_1=C_2 , E≠ 0 a small potential is developed across the membrane, it is calledas *asymmetric potential (E_{asy}).*



Cell representation: Ag / AgCl / HCl (0.1M) / unknown solution/ Glass

Working:

E_1& E_2 is the potential developed at outer and inner membrane respectively the boundary potential is, $E_b = E_2 - E_1$

$$E_b = E^0 + \frac{0.0591}{n}\log[C2] - \left\{E^0 + \frac{0.0591}{n}\log[C1]\right\}$$

$$E_b = \frac{0.0591}{n}\log[C2] - \frac{0.0591}{n}\log[C1]$$

$$E_b = \frac{0.0591}{n}\log[C2] + \frac{0.0591}{n}log\frac{1}{[C1]}$$

Where $L = \frac{0.0591}{n}log\frac{1}{[C1]}$

Therefore

$$E_b = L + \frac{0.0591}{n}\log[C2]$$

Here n=1, [C2] = $[H^+]$ ions in outer membrane, Then

$$E_b = L + 0.0591\log[H^+]$$

$E_b = L - 0.0591p^H$ (pH= -log$[H^+]$)

The Glass electrode potential is given by

$$E_G = E_b + E_{Ag/AgCl} + E_{Asy}$$

Substitute the value of E_b

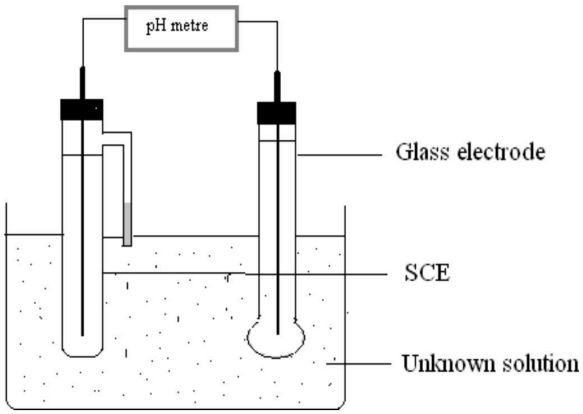
$$E_G = L - 0.0591p^H + E_{Ag/AgCl} + E_{Asy}$$

Consider$L_1 = L + E_{Ag/AgCl} + E_{Asy}$, Therefore

$$E_G = L_1 - 0.0591p^H$$

Determination of pH of a solution using Glass Electrode

The potential of a glass electrode depends on the concentration of H^+ ions. Hence, pH of a solution can be determined by using glass electrode and calomel electrode assembly.
The cell assembly is represented as
$Hg/Hg_2Cl_2/Cl^-$ // solution of unknown pH / glass/0.1 M HCl / AgCl / Ag



The emf of a cell is determined by using voltmeter.
E_{cell} is the difference b/w glass electrode potential E_G and the calomel electrode potential E_{SCE}.

$$E_{Cell} = E_{Cathode} - E_{Anode}$$

$$E_{Cell} = E_G - E_{SCE}$$

$$E_{Cell} = L_1 - 0.0591p^H - E_{SCE}$$

$$p^H = \frac{K - E_{Cell}}{0.0591} \qquad [K = L_1 - E_{SCE}]$$

Where K= Electrode assembly constant.

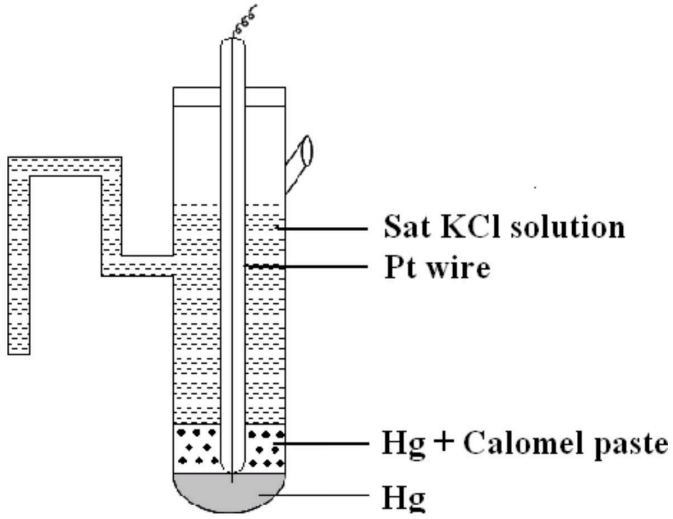
Reference electrodes

Reference electrodes are the electrodes whose potential is known and used for determination of potential of unknown electrodes

Calomel Electrode:

Construction:

1) Calomel electrode consists of long glass tube with two side tubes.
2) One at the top to fill saturated KCl solution and the other side tube is connected to the salt bridge. Mercury is placed at the bottom which is covered with a layer of Hg and Hg_2Cl_2 (calomel) paste.
3) The remaining portion is filled with saturated KCl solution.
4) A platinum wire is dipped into the mercury and is used to provide external electrical contact.



The calomel electrode is represented as, **$Cl^-/Hg_2Cl_2/Hg$**

Working:

Calomel electrode behaves as anode or cathode depending upon the nature of another electrode. The half-cell reaction when it acts as an anode is

$$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$$

The half-cell reaction when it acts as a cathode is

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

The electrode reaction is,

$$Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-$$

Applying Nernst equation,

$$E = E^0 + \frac{0.0591}{n} log \frac{[Reactants]}{[Products]}$$

$$E = E^0 + \frac{0.0591}{n} log \frac{[Hg_2Cl_2]}{[Hg]^2[Cl]^{2-}}$$

Since $[Hg_2Cl_2] = [Hg]^2 = 1$, the above equation becomes

$$E = E^0 + \frac{0.0591}{2} \log \frac{1}{[Cl^-]}$$

The calomel electrode potential is depending on the concentration of chloride ions in KCl. If the Concentration of chloride ions increases, the potential decreases and vice versa. (The potential of calomel is inversely proportional to the concentration of chloride ions)

The potential of calomel electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.334V	0.281V	0.242V

Applications:

1) Used to determine the potential of the otherelectrodes.
2) It is commonly used as reference electrode in all potentiometricdeterminations.

Electrolytic Concentration Cell:

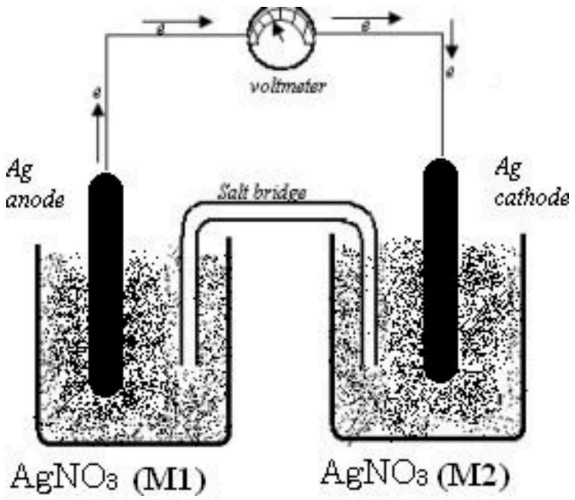
It is galvanic cell, which consists of two identical electrodes, which are in contact with the same solution of electrolyte in different concentrations.

Example:

Consider two silver electrodes that in contact with the $AgNO_3$ solution of different concentrations (M_1 and M_2) connected through voltmeter. The electrolytes are connected through salt bridge.

The cell representation Ag/ $AgNO_3$ (M_1)// $AgNO_3$ (M_2)/Ag

Where M_1 and M_2 are the molar concentration of the Ag^+ ions in the two half-cells.



$At\ Anode: Ag \rightarrow Ag^+(M1) + e^-$
$At\ Cathode: Ag^+(M2) + e^- \rightarrow Ag$
$Net\ Cell\ Reaction: Ag^+(M2) \leftrightarrow Ag^+(M1)$

Apply Nernst equation for the cell reaction,

$$E = E^0 + \frac{0.0591}{n} log \frac{[Reactants]}{[Products]}$$

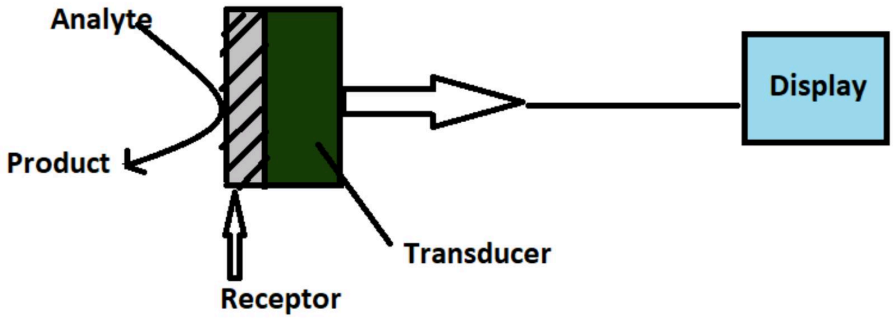
$$E^0 = E^0{}_{Cathode} - E^0{}_{Anode}$$

Since both anode & cathode is made up of same metal, $E^0 = 0$

$$E = 0 + \frac{0.0591}{n} log \frac{[M2]}{[M1]} \qquad or\ E = \frac{0.0591}{n} log \frac{[M2]}{[M1]}$$

SENSORS

A sensor is a device that detects and responds to some type of input from the physical environment.



Schematic diagram of components of sensors

Components of Sensors:

1. **Receptor:** it is a chemical element which is capable of interacting with analyte specifically and selectively. It produces signal corresponding to interaction in the form of change in potential, conductivity heat, pH etc.
2. **Transducers:** Transducers is used to convert the signal created by the receptor-analyte interaction into a readable value.
3. Electrical signals and Display.
4. The electronic system analyses the signal given by the transducer, converts the signal into digital form. These signals are then displayed.

Electrochemical Sensors:

These sensors use electrode as transducer component. The main components of electrochemical sensors are working or sensing electrode, electrolyte, counter and reference electrode. Electrolyte is a part of the electrochemical Sensors and role is to transport charge within the sensors, contact all electrode effectively, it is stable under all conditions.

Following steps are involved in working of an electrochemical sensor

1. Diffusion of the analyte to the electrode/electrolyte interface (in the liquid form)
2. Adsorption onto the electrode surface
3. Electrochemical reaction with electron transfer
4. Desorption of the product
5. Diffusion of the products away from the reaction zone to the bulk of electrolyte or gas phase.

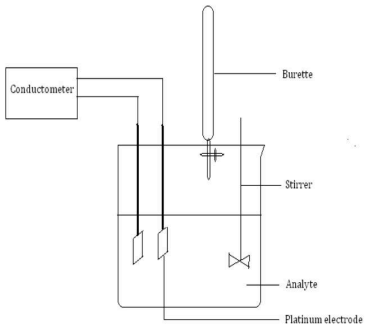
Applications:

1. The oxygen sensors are used to determine dissolved oxygen in boiler water and to monitor dissolved oxygen concentrations in hydrogen fuel cell.
2. Used in security and defence applications like detection of toxic gases.
3. Used in water analysis and environmental monitoring.
4. Used in diagnostic and health care applications.
5. Used in soil parameter analysis and in agricultural applications.

Note: Types of electrochemical sensors

1. Potentiometric Sensors:
   In this sensors change in potential during chemical interaction between receptor and analyte is measured using indicator electrode and reference electrode. Indicator electrode is used to measure the change in the potential due to redox reaction occurring on the surface of the electrode.
2. Amperometric Sensors:

Conductometric Sensors



It involves the determination of the concentration of analyte based on the measurement of changes occur in electrolyte solution. Conductance is depending on

- ✓ No. of ions
- ✓ Mobility of ions

Electrode used is conductivity cell. It is made up of two platinum foils with unit cross sectional area and unit distance between them. Conductance of unit volume of the solution is called specific conductance and it is given by

$$k = \frac{1}{R} \times \frac{l}{a}$$

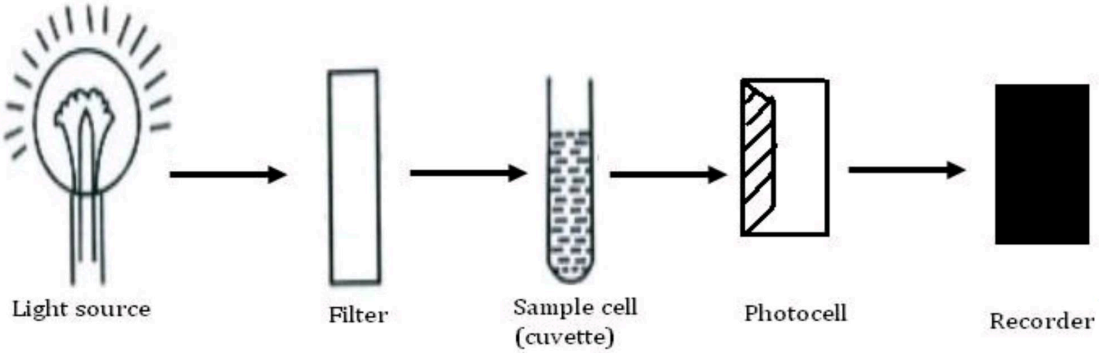
Here l/a is known as cell constant, R is resistance.

Applications:

1. Used to estimate acid, base and mixture in the sample
2. Used to check ionic impurities in water sample
3. Used to measure acidity or alkalinity of sea water and fresh water
4. Conductometric biosensors are used in biomedicine, environment monitoring, biotechnology and agricultural related applications.

Optical Sensors:

1. These sensors based on the interaction of electromagnetic radiation with the chemical species. Commonly UV-Visible-Infrared electromagnetic radiations are used. In an optical sensor, the optical signal arises from the interaction of the analyte with an incident radiation. This interaction could results in absorption, emission, scattering and reflection of light. The intensity of the radiation gives the information on the concentration of the analyte.
2. Optical sensors are used to determine the concentration of coloured solution. It is based on the measurement of absorbance of the coloured solution at particular wavelength. It is governed by Beer-Lambertz law.
3. The optical sensors components are light source, filters, photocell and display system.
4. Schematic diagram is as follows



Applications:

- Used in the determination of any chemical species which can interact with electromagnetic radiations
- Can be used in environmental, pharmaceuticals, food related applications

Thermometric Sensors:

It is based on the measurement of thermal changes during the interaction between analyte and receptor.

Working:

Main component is a small tubular catalytic reactor fitted with a temperature transducer. Analyte is fed into the reactor. The wall of the reactor is coated with a catalyst which is capable of catalyzing the reaction, liberating the heat energy. Heat liberated is quantified by transducer and convert into voltage and fed to the data storage and processing unit.

The two main transducers which convert change in temperature into an electric signal are

1. **Resistive transducers:** Most commonly used resistive transducer is the thermistor. It is a semiconductor device made up of oxides of transition metals.
2. **Thermocouple:** It is a device which converts the temperature difference into an electrical voltage.

Applications:

Used in determination of metabolites, bioprocess monitoring and environmental control and determination of combustible gases.

ANALYTICAL TECHNIQUES

COLORIMETRIC METHOD

Introduction: this method is useful to determine the concentration of unknown solution. The concentration of the unknown solution is determined by measuring the absorbance of the light radiations w.r.t known concentration. The instrument name is Photoelectric Colorimeter

Principle: The colorimeter is explained by Beer – Lambertz Law.

When a monochromatic light is passed through a solution, a part of light is absorbed by the solution. The absorbance depends on the concentration of the solution and the path length of the light through the solution.

Beer-Lambert's law: Absorbance is directly proportional to concentration and thickness.

$$A = € ct$$

€ = molar absorption co-efficient A = Absorbance of light, T = Path length, C = Concentration of the solution

Instrumentation: The instruments is used to measure the absorbance of a solution is called photoelectric colorimeter. It consists of

Source: tungsten bulb or lamp is used as a light source

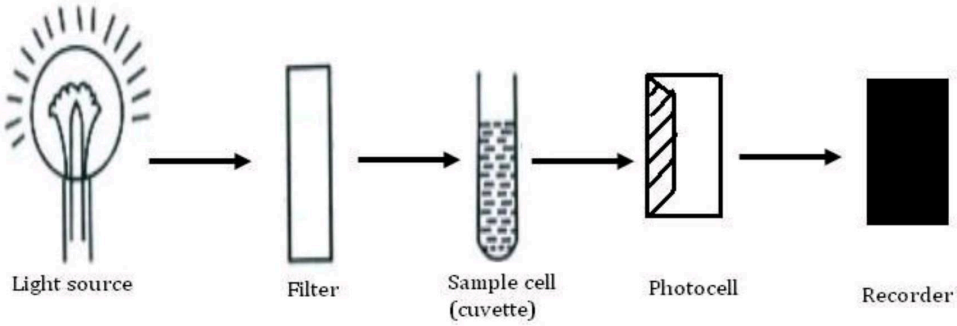
Filter: It is a device to provide desired wavelength range

Sample cell: Sample is hold in glass cell

Photocell: Converts the emitted light into electrical signal.

When light is allowed to fall on the sample cell at particular wavelength. The blank solution is taken in the sample cell and placed in the path of light beam. Its absorbance is adjusted to zero. Then the analyte solution I placed in the path of light and its

absorbance is measured. A plot of absorbance against standard concentrations of analyte is used to find the unknown concentration of analyte in the samples.

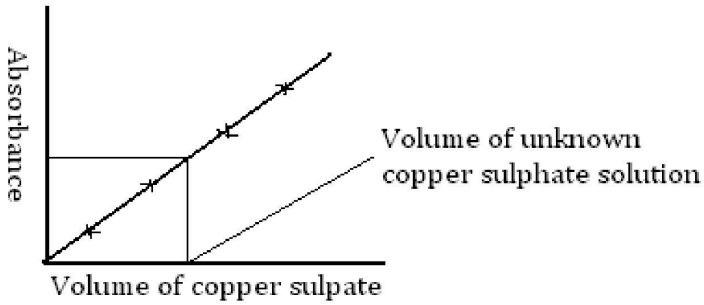


Applications:

- Inquantitative analysis: large number of metal ions, anions and cations compounds can be determined by in this method.
- Photometric Titration i.e. equivalence point can also be determined.
- Determination of the composition colored complex, blood analysis, urine analysis.

For example:

Procedure: Pipette out 2, 4, 6, 8, 10 ml of standard copper sulphate solution into 25 ml standard flask. Add 2.5 ml of ammonia solution into each of them and make up to the mark with distilled water and shake well. Set the filter to 620 nm. Adjust the initial reading to zero by using blank solution in the sample tube. Measure the absorbance for each standard flask solution and plot graph of absorbance v/s concentration of copper sulphate.



Advantages:

- Can be determine the concentration of the colored solution
- It is very simple method
- Colorimeter gives most accurate value
- Used for lower concentration

Potentiometric Titration

Aim: Determination of the weight of ferrous ammonium sulphate and ferrous iron in the given solution by potentiometric titration method.

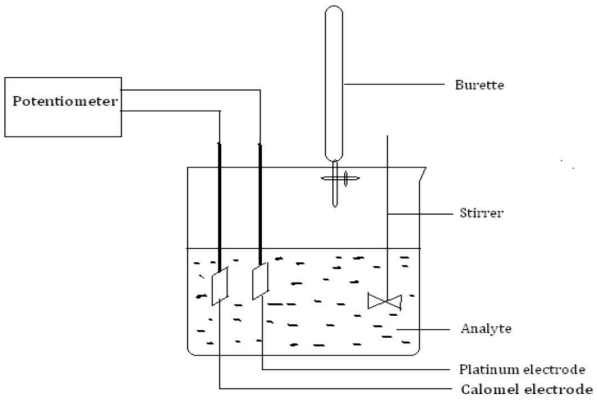
Theory: In this titration the amount of substance in the solution is determined by measuring the emf between two electrodes that are dipped into the solution. When the metal M is immersed in the solution containing its own ions M^{n+} ions, the electrode potential is given by Nernst equation,

$$E = E^0 + \frac{0.0591}{n} log[M^{n+}]$$

From this equation the potential of the electrode is directly proportional to the concentration of the ionic species present in the solution.

Instrumentation:

A potentiometer consists of a indicator electrode (e.g.: Platinum) and an saturated reference electrode (E.g.: Calomel electrode), stirrer & potentiometer to measure the potential values.
Emf of the solution can be measured by combining reference electrode with indicator electrode.



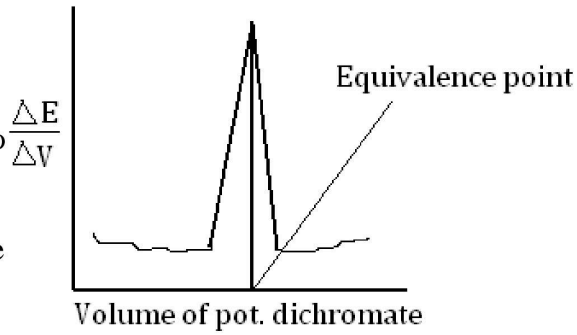
The electrode which responds to the change in the concentration of the ion in the solution is called indicator electrode & reference electrode is one whose potential is constant. A known volume of the analyte is taken in beaker and its potential is measured. The titrant is added in increments of 0.5ml and potential is measured each time. Near the equivalence point there is a sharp increase in the potential. The end point is determined by plotting change in potential against volume of the titrant.

Applications

1. Estimation of concentration of the ionic species present in the givensolution.
2. Coloured solution can also betitrated
3. Acid-base titration can also be done in thismethod.
4. In this method Oxidation-reduction titrations can also be carriedout.
5. Precipitation reactions can also be carried outpotentiometrically.

For example:

Procedure: Pipette out 25cm^3 of FAS solution into a 50 cm^3 beaker. Add one test tube full of dil H_2SO_4. Immerse Pt. & calomel electrodes into the solution, & connect the electrodes to a potentiometer. Fill the burette with $K_2Cr_2O_7$ solution. Add $K_2Cr_2O_7$ solution from the burette with increment of 0.5cm^3, stir well and measure the potential after each addition. Continue the titration till the potential indicates a rapid jump with a drop oftitrant. Plot the graph of $\Delta E/\Delta V$ v/s vol. of $K_2Cr_2O_7$.



Conductometric Titration

Conductance is ease with which current flows through the solution. It is reciprocal of resistance.
$C=1/R = \Omega^{-1}$ or mho or siemen

Theory:

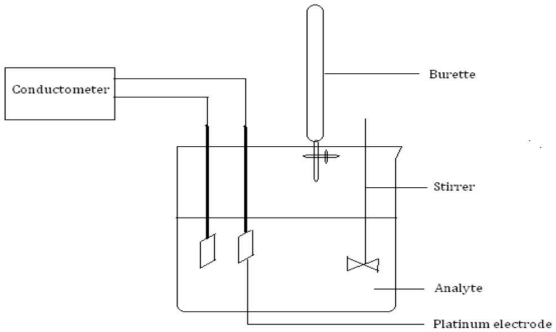
The Conductance of the solution is explained by considering ohm's law.
According to ohm's law the current flowing through the conductor is directly proportional to voltageand inversely proportional to the resistance.

$$I=\frac{E}{R} \text{ or } \qquad E = I\,R$$

The resistance of the any conductor is directly proportional to the length, inverselyproportional to the area of cross section of the conductor Therefore R = S (l/a) where S is specific resistance

Therefore C = 1/R =1/S(a/l), K(a/l), K = specificconductance
It is defined as the conductance of the solution present between two parallel electrodes of $1cm^2$ area of cross section and 1cm apart.
The conductance of the solution is depending on mobility of the ion and number of the ion.

Instrumentation:
It consists of two platinum electrodes each of unit area of cross section placed at unit distance apart. The electrodes are dipped in the electrolytic solution taken in a beaker. It is connected to a conductometer to measure the conductance. The conductance is measured after the addition of the titrant at interval of 0.5 ml.



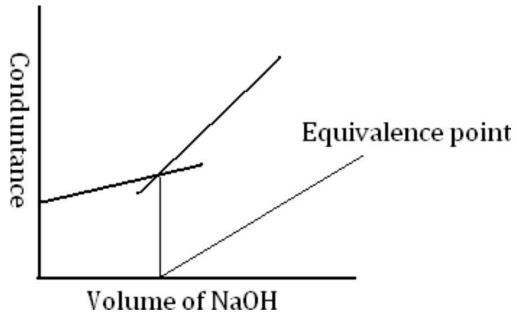
Types of conductance: There are three type's namely specific conductance, equivalence conductance, and molar conductance.
Specific conductance (K) is the conductance of the solution present between two parallel electrodes of $1cm^2$ area of cross section and 1cm apart.
K = 1/R (l/a) K = Siemen m^{-1}
Equivalence conductance (λ) is the conductance of the solution when 1g equivalent weight of solution is placed between two electrodes of area $1cm^2$ at 1cm apart.
Molar conductance (μ) is the conductance of the solution when 1g molecular weight of solute is placed between two electrodes of area $1cm^2$ at 1cm apart

Application of Conductometric titration
It is used in the estimation of acids and bases present in the sample solutions. The possible combinations and conductance responses are explained below,

Weak acid v/s Strong base (CH_3COOH v/s NaOH)
Consider the titration of acetic acid against NaOH. The conductance of the acid will be initially low since acetic acid is a weak electrolyte. When NaOH is added to the acid, the salt formed is highly ionized and the conductance increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile OH^- ions. Hence the conductance increases sharply.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



****