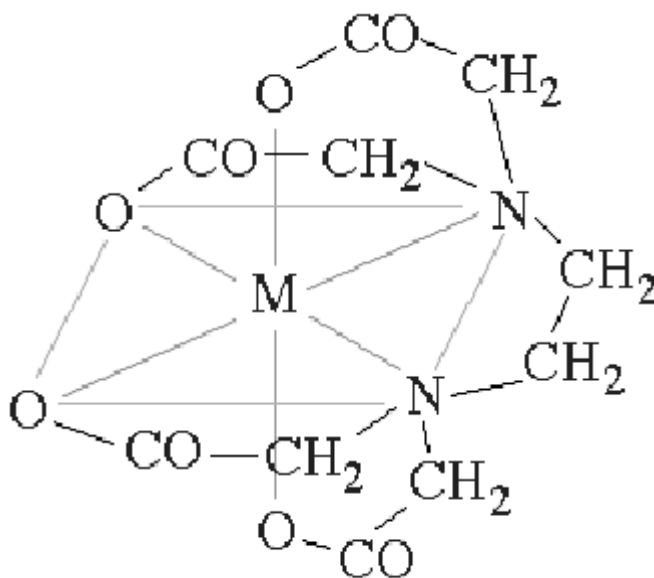
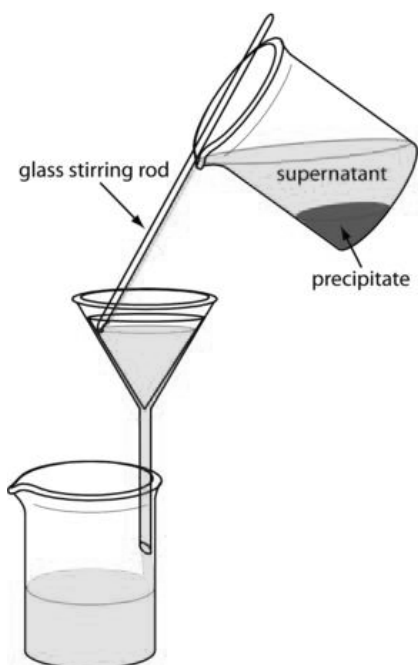
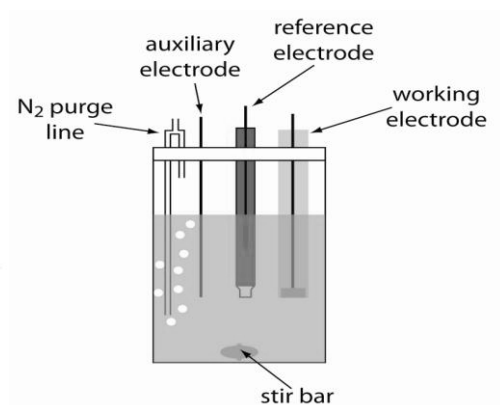
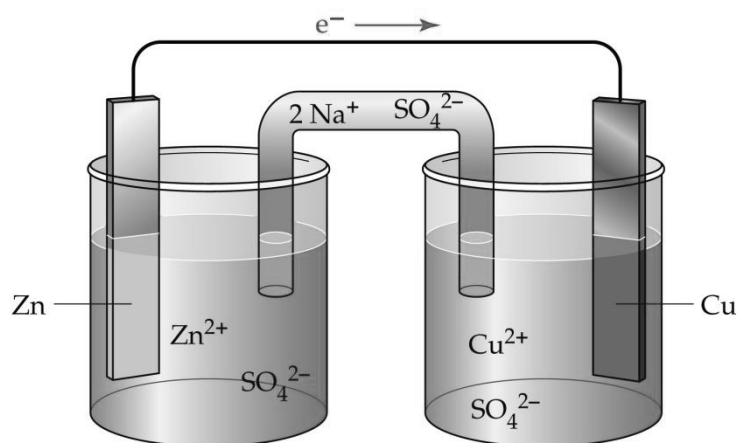




PHARMACEUTICAL ANALYTICAL CHEMISTRY II



Electrochemistry (Instrumental Analysis)

- **There are physicochemical methods of analysis in which we measure some electrical quantity or property of a solution to be analyzed qualitatively or quantitatively. The measurements are carried out by using certain instruments. (Instrumental methods of analysis)**

Advantages of electrochemical methods of analysis

- 1- Short time for analysis**
- 2- Used when classical methods of analysis cannot applied e.g.**
- 3- in case of closed, turbid, very dilute solution and when there is no available indicator**

Classification of electrochemical methods:

1- Conductometry and electrophoresis:

These methods depend on movement of ions in electric field, leading to conductance of electricity without occurrence of redox reaction at the electrode surface (no-electron transfer)

2. Potentiometry and polarography:

These methods depend on measuring voltages or current between two electrodes, where redox reaction take place at electrode surfaces (i.e electron transfer occurs at electrode surfaces).

- Some electrochemical definitions and units :
- a) Ampere :

It is the unit of current strength. It is a measure of the number of charges flowing through a conductor/second.

- a) Ohm :

it is unit of electrical resistance (R) . It is that resistance through which a difference in potential of one volt will produce a current of one ampere.

- c) Ohm⁻¹ (Semen) :

It is the unit of conductance (G).

- d) Volt (V) :

It is the unit of potential difference. It is the potential required to produce a current flow of one ampere through resistance of one ohm.

I. Conductometry

- **This method based on measuring electrolytic conductance.**
- **Conducance is the ability of electrolytic solution to carry the electric current.**
- **Electric current pass through metallic conductors e.g. iron wire or copper wire in the form of electron flow. But conduction of electricity through an electrolytic solution involves migration of cations towards cathode and anions toward anode i.e. current are carried by all ions present in solution.**

I. Conductometry

Conductance (G) of a solution is a reciprocal of its resistance i.e.

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

- G is conductance and
- R is resistance.

- Unit of resistance = ohm

- Unit of conductance = ohm⁻¹ or seimen

The conductance of electrolytic solution depend on:

1 -Nature of ions

The velocity by which ions move towards the electrode carrying the electric current varies according to their nature i.e charge, size and hydration.

- Velocity of ions $\propto \frac{1}{\text{charge}}$
- $\propto \frac{1}{\text{size}}$
- $\propto \frac{1}{\text{Hydration}}$

2-Temperature

- **Conductance is increased by increase of temperature as viscosity and hydration are decreased. An increase of temperature by 1°C is accompanied by 2% increase in conductance.**

3- Ions concentration

- **Conductance is directly proportional to the ions concentration**

4- The size of electrodes.

- **The conductance of electrolyte (G) is directly proportional to surface of electrode (A) and inversely proportional to the distance between the two electrodes (L)**

- i.e. $G \propto A$
- $G \propto \frac{1}{L}$
- $G \propto \frac{A}{L}$
- Or $G = K \frac{A}{L}$
- **K is proportionality constant, known as specific conductance or conductivity.**

Specific conductance (K)

- It is the conductance when L is unity (1cm) and A is unity (1 cm²)
or it is the conductance of cube of liquid

L

$$k = G \times \frac{L}{A} = \text{ohm}^{-1} \cdot \text{cm}^{-1} \text{ or } \text{semin } 1 \text{ cm}$$

A

K is constant for specific solution, but it is changed with concentration, temperature and change in cell constant.

Equivalent conductance:

- It is the conductance of one gm equivalent of solute contained between two electrodes spaced one centimeter apart.

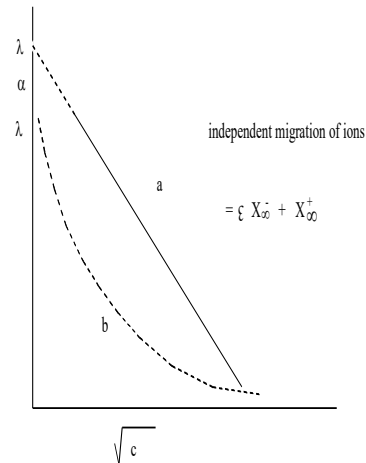
- Equivalent conductance (λ) = $\frac{k}{c} \times 1000$

C = concentration in gm equivalent per liter

- It is used to express the ability of individual substance to conduct electric current.

- **From the previous equation**
equivalent conductance is inversely proportional with concentration, until it reaches a constant limiting value at infinite dilution which is known as limiting equivalent conductance (λ_{∞}) or mobility which is characteristic for each substance.

- **From the curve**
- **a = for strong electrolyte there is linear relation between λ & \sqrt{c}**
- **equivalent conductance.**
- **b= For weak electrolyte there is non linear relation between λ & \sqrt{c} .**
- **c= concentration gram Ea/pe liter.**



- **N.B.**
- **During conductance determinations, there is no oxidation or reduction at the surface of electrodes, therefore we have to use inert electrodes e.g. pt.**
- **We must use alternative current (A-C) to avoid electrolysis of the sample to be analysed and prevent polarization of the electrodes.**

- Instrument used in conductometric determinations
- To carry out a conductamtric measurement, it is necessary to measure the resistance (R) of the solution where

- Conductance $G = \frac{1}{R}$

The instrument consist of two parts:

- 1- Conducment cell. It is the in which the solution to be determined will be filled.
- 2- Conductivity bridge (Kohlrausch bridge) which is formed from:
 - i) Wheatstone bridge
 - ii) An oscillator (to produre Alternative current (A.C) from direct current (D.C)

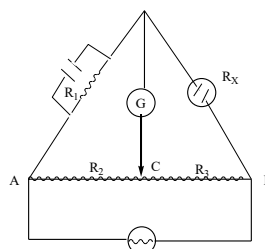


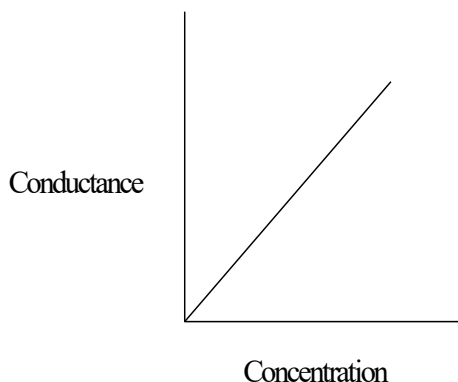
Fig. (3) Schematic diagram of conductivity bridge (conductivity meter)

Applications of conductometry

1) Direct conductometry

- **This method is used in industry for checking purity of distilled water or other chemicals and determination of some physical constants e.g ionization constant.**

- **In this method, a calibration curve is constructed by plotting the conductance of a series prepared from extra pure grade of the substance to be analyzed versus concentration. The conductance of the sample is measured and then its concentration is obtained from the calibration curve.**



2) Indirect conductometry (Conductometric titrations)

- **A conductometric titration involves measurement of the conductance after successive addition of titrant. The end point is obtained from a plot of conductance against ml. titrant.**
- **The most important advantages of this method are:**
 - I) **It can be used for determination of turbid and highly colored solution.**
 - II) **Very dilute solutions**
 - III) **It can be used when reaction is not complete and when there is no suitable indicator e.g. during weak acid, weak base titration.**

Precaution to be considered during conductometric titrations.

1. **The titrant used must be at least 10 times concentrated as the solution to be titrated e.g titration of 0.01 N HCl should be against 0.1 N NaOH (titrant). By this way we can minimize (decrease) in conductance due to dilution.**
2. **Avoid the presence of extraneous ions, which will increase initial conductance i.e change in conductance during titration cannot be accurately observed e.g in case of addition of buffer to the titrated solution .**
3. **The method is not suitable for detection of end point of redox reactions as there is no electron transfer at electrode surface during conductometric determination.**

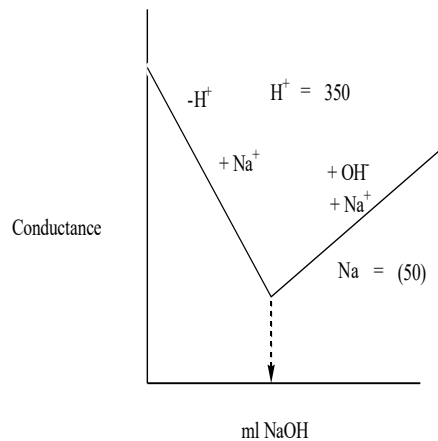
Examples of conductometric titrations

1-Acid-Base Titration

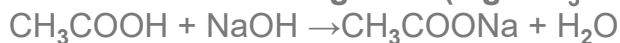
a-Strong acid \neq strong base (e.g. HCl \neq NaOH)

- $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- $\text{H}^+ + \text{Cl}^- + \text{Na}^+ + \text{OH}^- \rightarrow \text{Na}^+ + \text{Cl}^- + \text{H}_2\text{O}$
- First H^+ present in acid sample cause high conductance. By addition of NaOH, OH^- will consume H^+ forming H_2O which doesn't conduct electricity. Therefore conductance will decreased during the progress of the reaction although H^+ is replaced by Na^+ (as H^+ has higher mobility (349.8) if compared with mobility of Na^+ (50.1)).

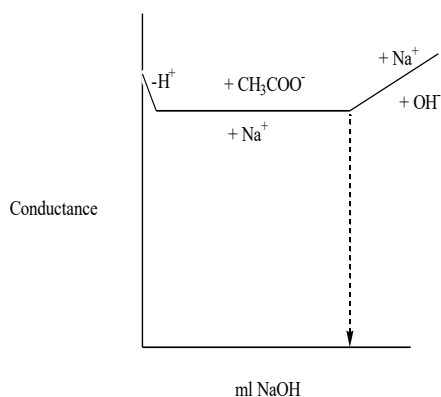
- After complete reaction excess NOH added will give free OH^- as well as Na^+ , therefore conductance is increased.
- Chloride ion (Cl^-) has constant effect on conductance as its concentration undergo no change during titration.
- The following figure represent conductametric titration curve of HCl \neq NaOH.



b. Weak acid \neq strong base (e.g. $\text{CH}_3\text{COOH} \neq \text{NaOH}$)



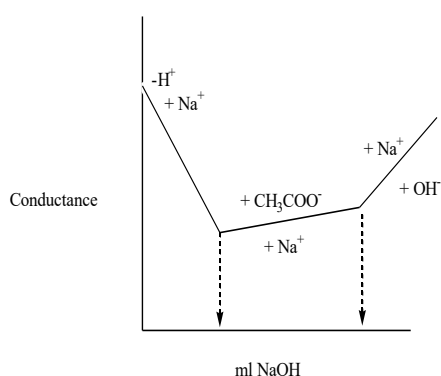
1. Before titration low initial conductance is observed due to low (H^+) obtained during dissociation of weak acid CH_3COOH . During titration we can observe slight decrease of potential due to consumption of initial H^+ during progress of titration we can observe slight increase in conductance due to the presence of CH_3COO^- & Na^+ and nearly constant (H^+) due to the buffer action of the produced CH_3COONa and the remaining CH_3COOH . After complete reaction excess NaOH will lead to increase in conductance due to increasing of Na^+ and OH^- after the end point.



c. Mixture of strong acid weak acid \neq strong base

e.g. $\text{HCl}/ \text{CH}_3\text{COOH}$ mixture $\neq \text{NaOH}$

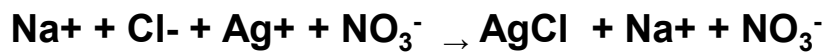
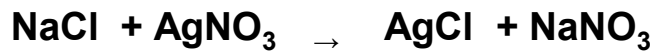
- The same principle of (a) and (b) can be considered during titration of $\text{HCl}/ \text{CH}_3\text{COOH}$ mixture $\neq \text{NaOH}$



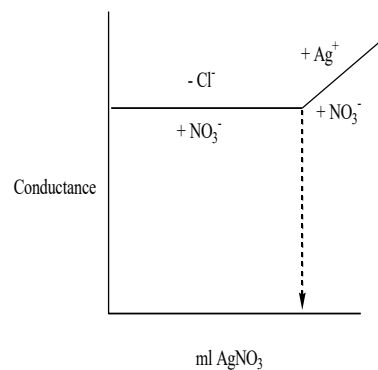
2. Precipitation titrations

- Examples:

- a) Titration of NaCl \neq AgNO₃



- During titration of NaCl against AgNO₃, Ag⁺ precipitate Cl⁻ as AgCl and NO₃⁻ replace Cl⁻ in the medium. As mobility of NO₃⁻ (71.5) is nearly equal that of Cl⁻ (76.3) we observe nearly no change in conductance during titration. After complete precipitation of Cl⁻ excess, Ag⁺ (61.9) and NO₃⁻ (71.5) will increase conductance of solution.

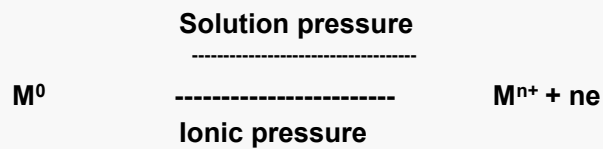


II. Potentiometry

- **Potentiometry is a measured of analysis used in the determination of ions or substances concentration by measuring the voltage (potential difference) developed between two electrodes, where electron transfer occurs at electrode surface**

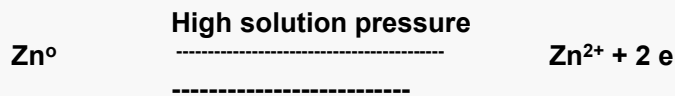
- **Electrons transfer from reductant to oxidant, in the same solution (i.e electrons transfer takes place in one phase) will produce electromotive force (E.M.F) which is known as **oxidation potential**.**
- **In some other cases transfer of electrons takes place between element and its ions (i.e electron transfer takes place between two phases. In this case E.M.F. produced is known as **electrode potential**.**

- Transfer of electrons between element and its ions depends on the nature of element; this can be represented by the following equilibrium.

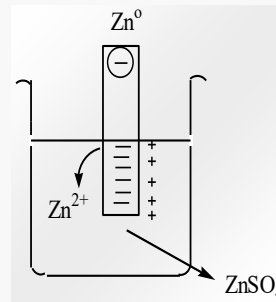


- According to the nature of metal, it may have:
 - The element has high solution pressure i.e. tendency to lose electrons and converted to its ions e.g. Zn⁰, Fe⁰, Co⁰, Ni⁰.
 - The element has high ionic pressure i.e. tendency to accept electrons and converted to elements e.g. Cu⁰, Hg⁰, Ag⁰

- When metal of high solution pressure is immersed in solution of its ions e.g. Zn⁰, Ni²⁺ the following equilibrium will be established.
- This can be represented by the following equilibrium.



- **Anodic half reaction (oxidation process)**
High solution pressure
E.M.F produced (electrode potential)
has a negative (-ve) signs



- **When metal of ionic pressure is immersed in solution of its ions e.g. $\text{Cu}^{\circ} / \text{Cu}^{2+}$ the following equilibrium will be established**

High ionic pressure

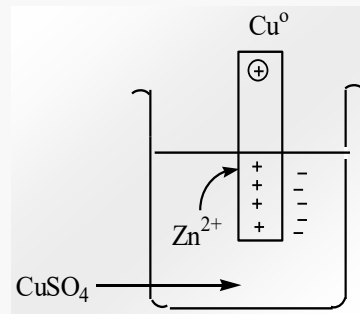
- $\text{Cu}^{\circ} \quad \text{-----} \quad \text{Cu}^{2+} + 2 e$
- **Cathodic half reaction (reduction process)**

Cathodic half reaction
(reduction process)

E.M.F produced

(electrode potential)

CuSO₄ has a positive
(+ve) sign



Calculation of electrode potential

- **Electrode potential can be calculated from Nernst equation**

– **Nernst equation for metal/ metal ion (Mo/Mn+)**

- $E_{25^{\circ}\text{C}} = E_0 + \frac{0.059}{n} \log [\text{Mn}^+] \text{ i.e. } E_{25^{\circ}\text{C}} \propto [\text{Mn}^+]$

- Where
- $E_{25^{\circ}\text{C}}$ = Electrode potential at 25°C
- E° = Standard electrode potential
- n = Number of electrons gained or lost
- $[\text{Mn}^{+}]$ = Molar concentration of metal ion.
- $[\text{Mn}^{-}]$ = Molar concentration of non-metal ion
- From Nernst equation $E_{25^{\circ}\text{C}}$ is a function of ionic concentration.
- When ionic concentration is 1 molar.
- $E_{25^{\circ}\text{C}} = E^{\circ}$ (i.e standard electrode potential)

Electrochemical cells

- Type of electrochemical cells.

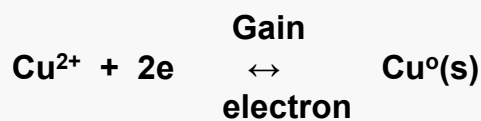
A) Galvanic cell : In this type the chemical energy is converted into electrical energy.

B) Electrolytic cell : In this type the electrical energy is converted to chemical energy

A) Galvanic cell

- Where the chemical energy is converted to electrical energy which can be supplied to an external circuit i.e. it produce electrical energy
- i) Voltaic cell (Danielle cell) $Zn^0/Zn^{2+} // Cu^0/Cu^{2+}$

- The copper electrode is the cathode.
The cathodic half reaction . the cathodic half reaction is :

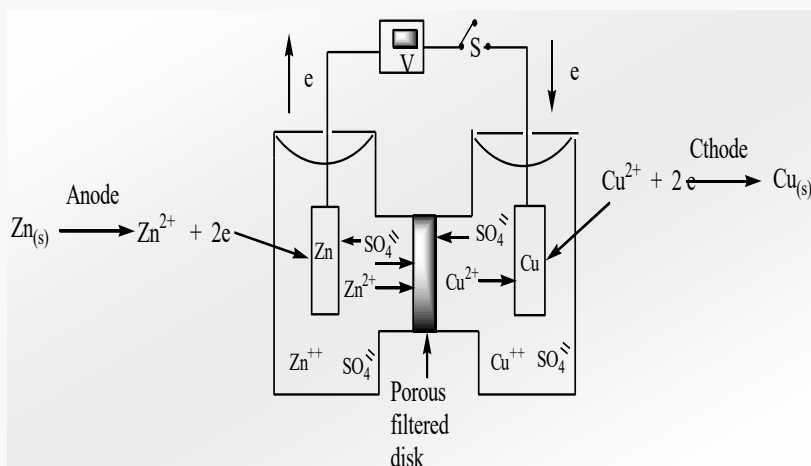


- The zinc electrode is the anode



- Electrons are supplied from the zinc electrode to the external circuit to the copper electrode and copper is deposited on the electrode surface. The two electrodes are connected by a junction which allows transference of by this way we have complete circuit.
- The potential difference i.e. electromotive force (E.M.F) of the obtained cell is
- $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$
- Where E_{cathode} and E_{anode} are the electrode potential of the cathode and anode.
- e.g. Danielle cell
 $E_{\text{cell}} = E_{\text{Cu}} - E_{\text{Zn}}$
 $E_{\text{cell}} = 0.34 - (-0.76) = 1.1 \text{ V}$

- A galvanic cell (Danielle cell) with liquid junction. Arrows show direction of flow of charge when S is closed.



- **N.B.**
 1. Cathode is electrode at which reduction takes place while
 2. anode is electrode at which oxidation takes place.

In this case $E_{cell} = E_{Cu^0} - E_{Zn^0}$

3. In galvanic cell electrons flow from anode to cathode.

- Salt bridge
- It is a liquid junction connect between the two half cell without mixing. Salt bridge may be in the form of bond tube or inverted U shape tube filled with agar gel prepared in saturated KCl or KNO_3 solution. Ions in salt bridge must not pass to the two half cell, this can be achieved by blocking the two ends of salt bridge with cotton wool or gelatin or agar.

- Liquid junction potential
- Sometimes potential is developed between the two boundaries of junction at the two ends of salt bridge, this potential is known as liquid junction potential. Liquid junction potential is produced due o the difference in the rates of migration of both cations and anions of the salt bridge which leads to unequal distribution of charges at the end of salt bridge thus producing a potential.

- To reduce liquid junction potential we have to:
 1. Choose the electrolyte of salt bridge, that its cations and anions have nearly the same mobility so that they move by the same rate, leading to equal distribution of charge e.g KCl or KNO₃ (K⁺ = 73.5, Cl⁻ = 76.3. NO₃⁻ = 71.5).
 2. Use of high concentration of electrolyte in salt bridge to reduce difference in rates of migration of ions.

- B) Electrolytic cell
- In this type external EMF is applied which is transformed to chemical energy. Daniel cell can be converted to electrolytic cell if we apply potential from external source opposing that of galvanic cell.
- $Zn^{2+} + 2 e = Zn^{\circ}$
- $Cu^{\circ} = Cu^{2+} + 2e$
- i.e. Copper electrode become the anode and zinc electrode become the cathode.

- Potentiometer
- Potentiometer consists of
 - 1) Galvanic cell :
 - 2) Voltage divider:

Classification of electrodes:

A) Classification of electrodes according to the type.

1. Electrode of first type.

- In this type, electrode potential depends on equilibrium between element and its ions (i.e. it is two phases electrode).

- (M⁰/Mn⁺)

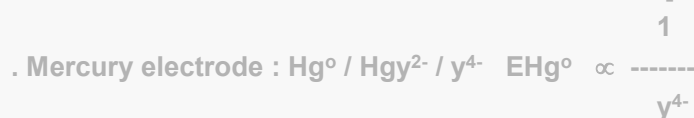
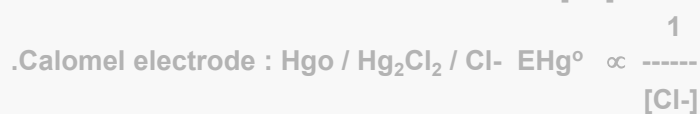


$$E = E_0 + \frac{0.06}{n} \log [Mn^+]$$

- Form Nernst equation $E \propto [Mn^+]$

2. Electrode of second type.

- In this type equilibrium is established between three phases e.g metal covered with a layer of its sparingly soluble salt immersed in a solution of electrolyte, its anion form sparingly soluble salt or weakly ionisable compound with metal ion.



3. Redox electrode:

- In this type equilibrium is established between oxidant and reductant in the same solution in presence of inert electrode e.g pt. wire. (i.e it is one phase system electrode)
- e.g. Fe³⁺ / Fe²⁺ in presence of pt.

$$E = E_o + \frac{0.06}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

i.e. E ∝ $\frac{[\text{Ox}]}{[\text{Red}]}$

-

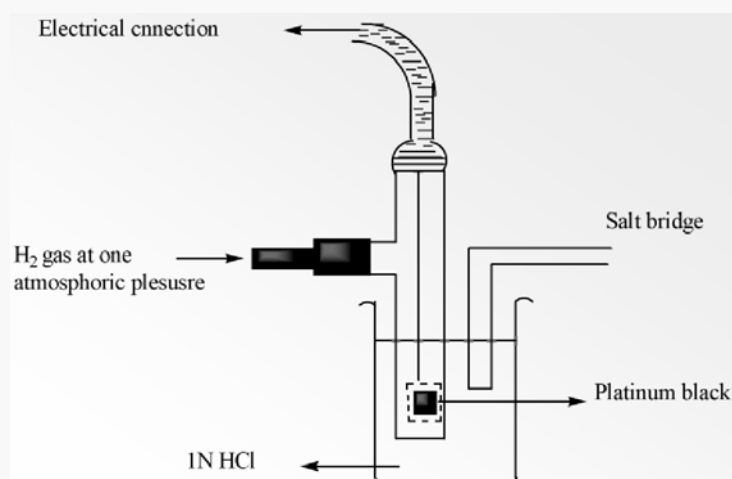
B) Classification of electrodes according to the function.

- **Electrodes can be classified according to the function as reference electrodes and indicator electrodes.**

1) Reference electrodes

- **Electrode has a known and constant potential and used to measure the potential indicator electrode through galvanic cell**
e.g. Normal hydrogen electrode (N.H.E), calomel electrode, silver electrode.

**a) Normal hydrogen electrode (N.H.E)
pt. $H_2 / H^+ (1N)$**



Normal hydrogen electrode (N.H.E)

- Electrode reaction :



0.06

- Nernst equation $E = E_o + \frac{0.06}{2} \log [\text{H}^+]^2$

$$\therefore E = E_o + 0.06 \log [\text{H}^+]$$

$$\text{i.e. } E \propto [\text{H}^+]$$

in N.H.E $[\text{H}^+] = 1$ as $\log 1 = \text{Zero}$

- $\therefore E = E_o = \text{Zero}$

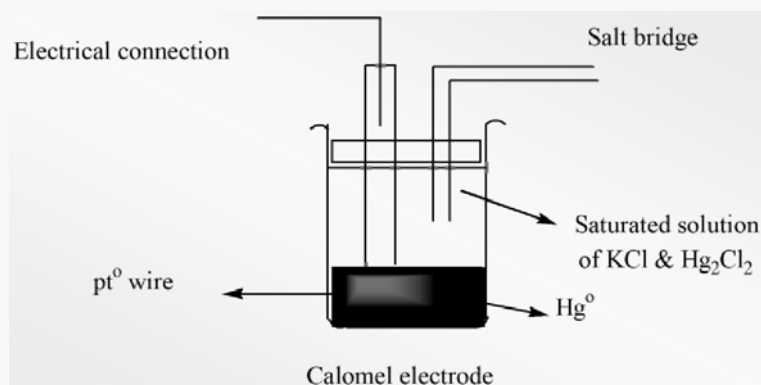
- Advantage of Normal hydrogen electrode (N.H.E)

It is a primary reference electrode and its potential is considered to be zero.

- Disadvantages of Normal hydrogen electrode (N.H.E)

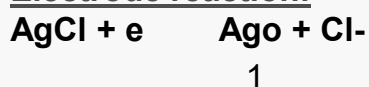
1. The presence of oxidant or reductant will interfere with the equilibrium or function of the electrode.
2. Catalytic poison e.g S^{2-} will interfere with the catalytic activity of pt black.
3. We cannot keep H_2 gas at one atmosphere during all determinations.
4. It needs replacing of pt black.

- **b) Calomel electrode (E = 0.28 volt)**
- $\text{Hg}_0 / \text{Hg}_2\text{Cl}_2 / \text{KCl}$ (saturated solution or 1N or 0.1N)
- **Electrode reaction:**
- $\text{Hg}_2\text{Cl}_2 + 2e = \text{Hg}_0 + 2\text{Cl}^-$
- $E_{\text{Hg}_0} \propto \frac{1}{[\text{Cl}^-]}$ (i.e. calomel electrode is Cl⁻ dependent)

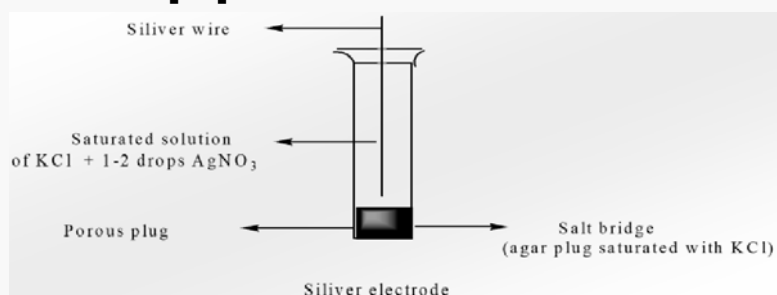


- **c) Silver electrode**
- $\text{Ag}_0 / \text{AgCl} / \text{KCl}$ (sat or 1N or 0.01N//)
- **(The same principle of calomel electrode)**

Electrode reaction:



- i.e. $E_{\text{Ag}_0} \propto \frac{1}{[\text{Cl}^-]}$ (i.e. Ag₀ electrode is Cl⁻ dependent)



2) Indicator electrodes

- **An indicator electrode**
 - (1) Is sensitive to the concentration of one of the reactants or product of reaction
 - (2) It must give rapid response
 - (3) Its response must be reproducible response.
 - These electrodes are classified into two classes
- A) **Metallic electrodes:** where redox reaction takes place at electrode surface.
- B) **Ion selective electrodes (or specific ion electrodes)** where charge exchange takes place at specific membrane surface

1- Electrodes used for redox reactions.

- **These are inert and accept the potential of the system in which they are dipped e.g platinum or gold in the form of coils or foil or plates to expose a large surface area to the solution to attain the equilibrium potential rapidly**

2- Electrodes used for precipitometry and complexometry)

a) Electrodes of first type (kind or order) e.g. Ag° for determination of Ag^+ , it is used for determination of $\text{Ag}^+ \neq \text{Cl}^-$, Br^- and CN^-

- Its potential is $E_{\text{Ag}^\circ} = E_o + 0.06 \log [\text{Ag}^+]$
- deformation of crystal structure and the presence of oxide coating

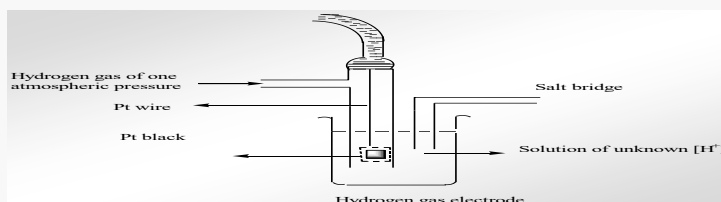
b) Electrodes of second type

- These are used for determination of anions. A metal electrode is indirectly responsive to anions that form sparingly soluble salt or stable complexes with its cations
- e.g. Ag° electrode : $\text{Ag}^\circ / \text{AgCl} / \text{Cl}^- //$
- i.e. Ag° coated with a layer of AgCl immersed in Cl^- sample.
- Its potential is $E_{\text{Ag}^\circ} = E_o - 0.06 \log [\text{Cl}^-]$
- Similar electrodes for Bromides and Iodides can be used.

3- Electrodes used for neutralization reactions

a) Hydrogen electrode.

- Electrode reaction $H^+ + e = \frac{1}{2} H_2$
- Nernst equation :
- $E = E_o + 0.06 \log [H^+]$
- = Zero + 0.06 log [H⁺]
- i.e E = - 0.06 pH
- When it is connected with N.H.E as reference electrode
- E cell = E reference – E indicator
- E cell = Zero – (- 0.06 pH) = 0.06 Ph
- Disadvantages
- As mentioned under N.H.E in addition to, it cannot be used for determination of pH of volatile acid e.g CO₂ at it will be bubbled out by H₂ gas



b) Quinhydrone electrode

- It is formed by addition quinone (Q) and hydroquinone (H₂Q) in equimolar proportions to the solution to be analysed and inert electrode (pt) is immersed in the solution.
- Electrode reaction :
- $Q + 2H^+ = 2e H_2Q$
- Nernst equation :
- $E_{Q/H_2Q} = E_o + \frac{0.06}{2} \log \frac{[Q] [H^+]^2}{[H_2Q]}$
- $E_{25oC} = E_o + \frac{0.06}{2} \log [H^+]^2$
- $E_{25oC} = E_o + 0.06 \log [H^+]$
- or $E_{25oC} = E_o - 0.06 \text{ pH}$

- Advantages of Quinhydrone electrode
 - 1- Easily prepared and used
 - 2- Not affected by catalytic poison
 - 3- It comes to equilibrium rapidly
 - 4- Can be used for determination of pH of volatile acids e.g CO₂
- Disadvantages of Quinhydrone electrode
 - 1- Cannot be used in presence of oxidizing and reducing agents.
 - 2- Cannot be used at pH > 8 because H₂Q react with alkali
 - 3- Atmospheric oxygen slowly oxidize H₂Q. therefore it must be freshly prepared.

c) Glass electrode

- It is one of the ion selective electrodes. Ion selective electrodes respond to activity (a) more than concentration of ions.

$$a = [Mn^+] F_a$$

- Where : [Mn⁺] = Molar concentration of ions
F_a = The activity coefficient
- Activity coefficient (F_a) varies with the ionic strength.

Glass electrode

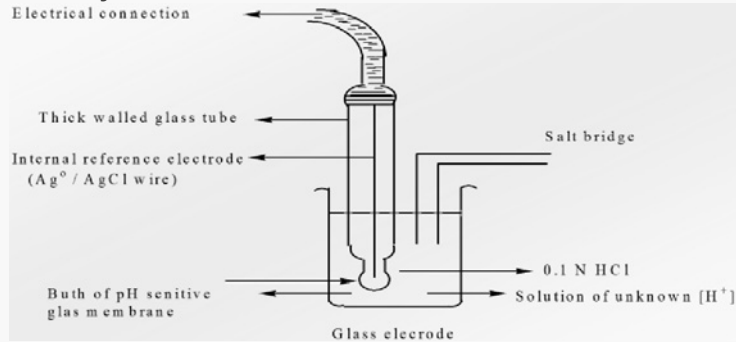
Ion selective electrodes.

Electrodes respond to activity (a) more than concentration of ions.

$$a = [Mn^{+}] F_a$$

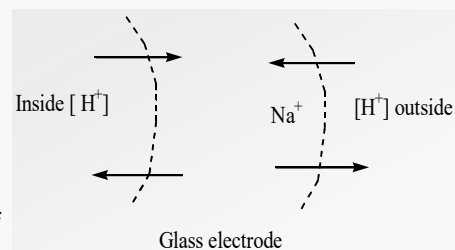
[Mn⁺] = Molar concentration of ions

F_a = The activity coefficient



Theory of operation of glass electrode :

- Potential is developed on the membrane due to the presence of different [H⁺] inside and outside the membrane. The potential is due to ion exchange between H⁺ and one of the component ions of glass matrix (e.g Na⁺). H⁺ is exchanged on both sides of the membrane depending on the different activities of solution inside and outside leading to charge imbalance and consequently potential development.



- The potential developed is represented by the following equation :
- $E = K - 0.059 \text{ pH}$
- Where : E = potential developed
K = asymmetric potential, E of two reference electrodes,
pH of internal solution and liquid junction potential.
- N.B.
- H^+ is exchanged in the form of H_3O^+ , therefore hydration of the membrane is necessary by keeping the membrane immersed in water. Also we have to avoid the use of glass electrode in presence of dehydration agent e.g Conc. H_2SO_4 and alcohol.

- Advantages of glass electrode

- 1- It can be used to measure the pH of solution containing oxidizing agents and reducing agents.
- 2- It can be used in presence of catalytic poison.
- 3- It can be used for determination of pH of volatile acids e.g CO_2

- Disadvantages of glass electrode

- 1- Cannot be used in presence of dehydrating agent
- 2- Fragile
- 3- Takes time to come equilibrium due to resistance of glass
- 4- Cannot be used above pH = 12 as Na^+ exchange together with H^+ leading to higher results.

Applications

Direct potentiometry

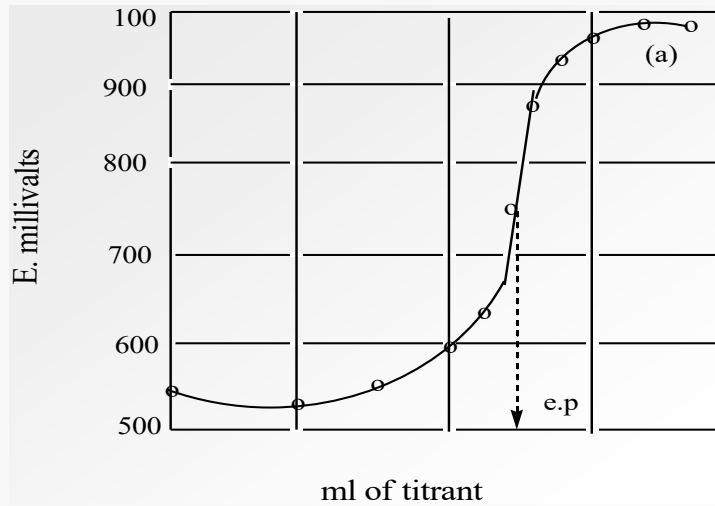
- **Direct potentiometric determinations depend on Comparing the potential of indicator electrode when immersed in the solution of substance to be analyzed and that of standard solution of the same substance.**
- **Calibration curve method in which we plot the potential of galvanic cell versus a series of standard solution prepared from extra pure grade of the substance to be analyzed. Then the potential developed when indicator electrode is immersed in solution of the substance to be analyzed is measured. From calibration curve we can obtain the concentration of the sample.**

Indirect potentiometry

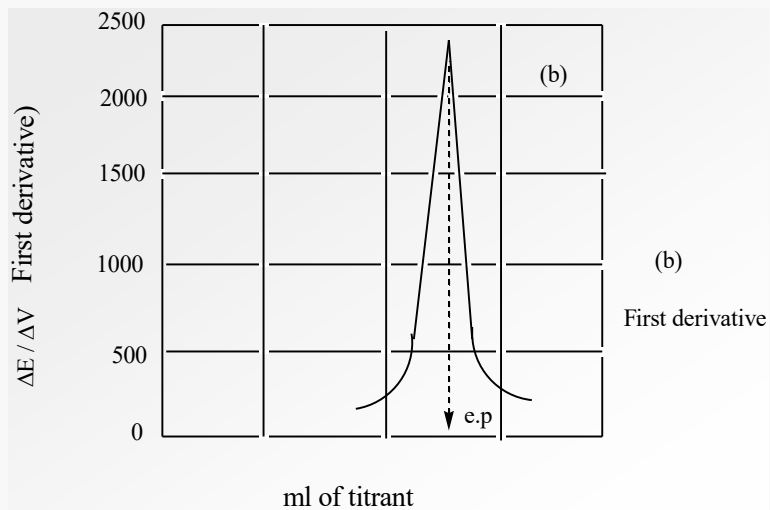
(potentiometric titration or potentiometric determination of end point)

- **It is the detection of end point during titration by measuring the change in the potential developed on indicator electrode immersed in the solution of the substance to be analyzed, then we plot.**
 - a) **Change in potential versus ml. titrant.**
 - B) **$\Delta E / \Delta V$ versus ml titrant (First derivative curve)**
 - c) **$\Delta^2 E / \Delta V^2$ versus ml titrant (Second derivative curve)**

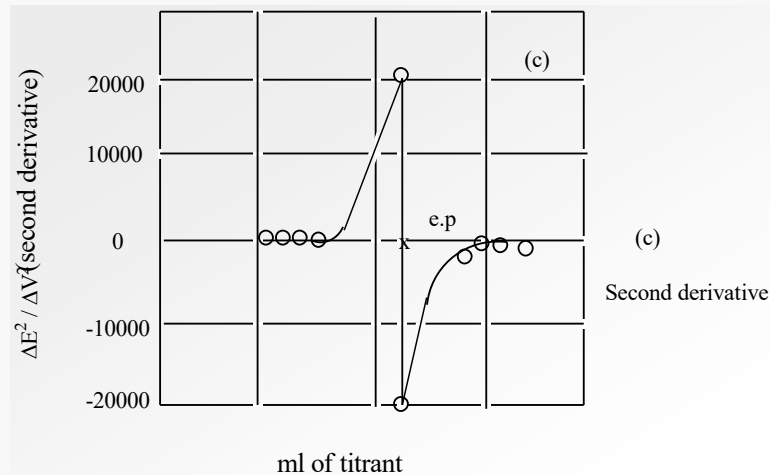
a) Change in potential versus ml. titrant.



**B) $\Delta E / \Delta V$ versus ml titrant
(First derivative curve)**



c) $\Delta^2E / \Delta V^2$ versus ml titrant
(Second derivative curve)



- **N.B**
- **Location of end point in**
- **(a) will dependent upon the skill, which the titration curve has been drawn through points plotted on the graph from the experimental observations. It is preferable to employ derivative methods of locating the end point, these consist of plotting first derivative curve**
- **(b) $(\Delta E / \Delta V)$ or the second derivative curve**
- **(c) $(\Delta^2 E / \Delta V^2)$ against the volume of titrant. The first derivative curve gives a maximum of inflection of the titration curve at the end point. Whilst the second derivative is zero at the end point.**

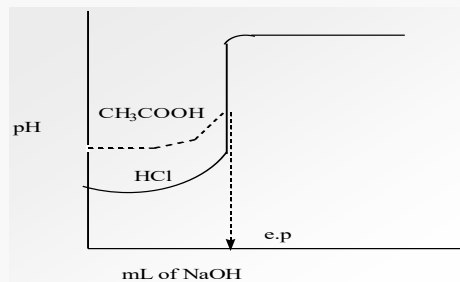
Application of potentiometric titrations

1) Neutralization reactions

Electrode system of galvanic cell is glass electrode (as indicator) // calomel electrode (as reference)

Instrument. pH-meter which is potentiometer, its millivolt (mv) scale is converted to pH scale by dividing the potential over 0.06.

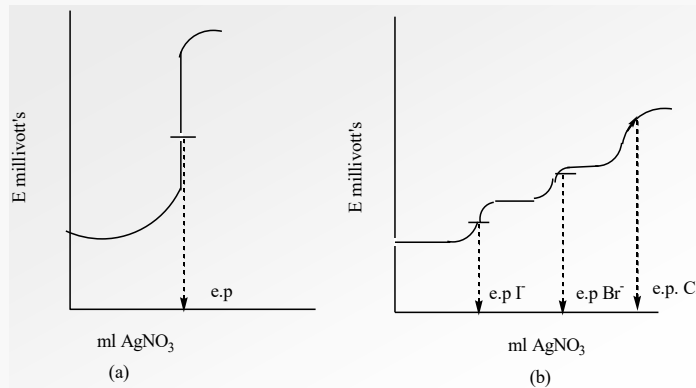
The titration curve is a plot of pH values obtained during the titration versus the volume of titrant.



2) Precipitation reactions

- **Electrode system of galvanic cell of galvanic cell, metallic silver electrode (as indicator) // calomel electrode (as reference electrode) this electrode system is used during argentometric determination of halides, halogenoides, sulphides, mercaptans, phosphates and oxalates.**
- **The titration curves obtained in determination of halide (Cl⁻) and mixture of halides (Cl⁻, Br⁻, I⁻) with silver nitrate are shown below.**

- (a) Potentiometric titration of chloride against AgNO_3
- (b) Potentiometric titration of Cl^- , Br^- , I^- mixture against AgNO_3



3- Complexation reactions

- e.g potentiometric titration curve of Bi^{3+} , Cd^{2+} and Ca^{++} against EDTA:
- Electrode system of galvanic cell $\text{Hg}^0 / \text{HgY}^{2-}$ (as indicator)// calomel electrode (as reference)
- Mercury electrode used as indicator electrode, is an electrode of the second type (or second order)
- $\text{HgY}^{2-} + 2 e = \text{Hg}^0 + \text{Y}^{4-}$
- As a second order electrode $E \propto \frac{1}{\text{Y}^{4-}}$
- A drop of 0.005 M HgY^{2-} is added to the solution to be determined before titration. After complete reaction between Y^{4-} and metal ion e.g Bi^{3+} , Cd^{2+} , Ca^{2+} etc., excess Y^{4-} will lead to sharp decrease in potential indicating the end point.

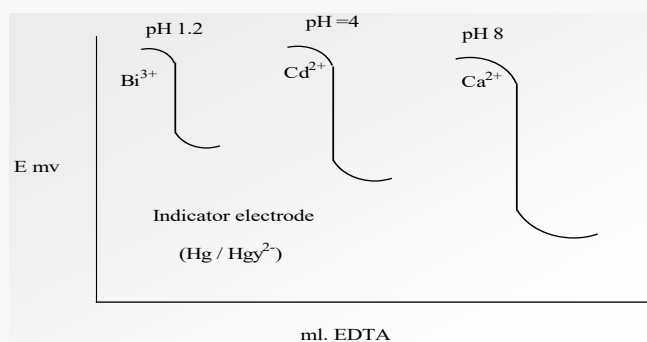
e.g Determination of Mixture of Bi^{3+} , Cd^{2+} and Ca^{2+}

1) Bi^{3+} at pH 1-2

2) Cd^{2+} at pH 4

3) Ca^{2+} at pH 10 using ammonia buffer.

- Potentiometric curve of Bi^{3+} , Cd^{2+} , Ca^{2+} against EDTA

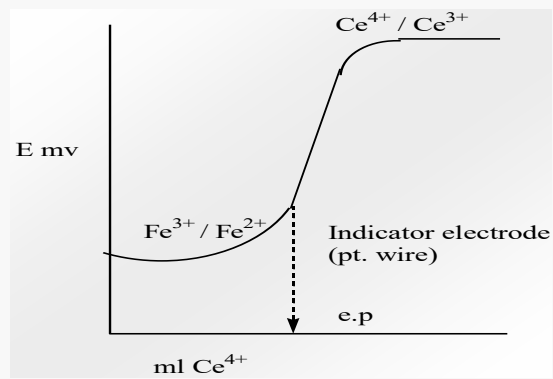


4- Oxidation-reduction reactions.

- **Electrode system of galvanic cell includes pt wire (as indicator electrode) immersed in the sample to be titrated which is sensitive to the ratio, where there is a large change in potential at the end point.**

e.g Titration of $\text{Fe}^{2+} \neq \text{Ce}^{4+}$
i.e $\text{Fe}^{3+} / \text{Fe}^{2+} \neq \text{Ce}^{4+} / \text{Ce}^{3+}$

Potentiometric titration curve of Fe^{2+} against Ce^{4+}



polarography

VOLTAMMETRY

Voltammetry is the technique which concerned with the study of voltage – current relationships during electrolysis in a cell,(Measurement of the current as a function of the applied potential)

Electrolysis : is the occurrence of chemical reaction under the influence of an electromotive force at electrode immersed in solution.

In voltammetry, the plot of the measured current as a function of applied potential is called voltammogram Basic instrument for voltammetric measurements. (polarogram)

Electrochemical cell for voltammetric study composed of three electrodes

Working (indicator) electrode: is the electrode at which oxidation or reduction of the analyte takes place. Its surface area is small and it is completely polarized e.g. dropping mercuric electrode (DME), solid electrodes like gold, platinum and carbon.

Reference electrode : has a potential that remain constant during measurements this electrode is larger in size relative to working electrode and non polarized (depolarized) e.g. Saturated calomel electrode (SCE)

Counter electrode: is used to complete the electrical circuit . It made from gold or platinum .

Supporting electrolyte: Solution of electrolyte not oxidized or reduced (not react) with electrodes but has conductivity of the solution e.g. KNO_3

Polarization : Suppose an electrode (cathode) having a small surface area immersed in a solution (containing metal ions M^+) with a second large electrode and a voltage is applied across the two electrode, the reaction $\text{M}^+ + \text{e} \longrightarrow \text{M}^0$ can take place at the small electrode

When the electrode has become polarized, a fresh supply of M^+ ions to its surface is controlled by the rate of mass transfer the metal ions from the bulk of the solution to the electrode surface .

Polarography

- **The polarographic method of analysis was first described by**
- **J. Heyrovsky in 1922.**
- **Polarography is a type of voltammetry in which working microelectrode is dropping mercury electrode (DME) and the counter electrode is a mercury pool.**

Polarographic measurements and principles.

In a polarographic analysis, the solution of the analyte is made a part of a special type of electrolytic cell containing a mercury microelectrode at which the analyte react. Measurement of the diffusion-controlled current flowing in an electrolytic cell in which one electrode is polarizable . The current is directly proportional to the concentration of an electro active species. Both qualitative and quantitative information is obtained from plots of the current generated in the cell as a function of applied potential.

Polarographic apparatus

For polarography, as well as the other voltammetric techniques, the working electrode is the dropping mercuric electrode (DME) as cathode at which the analyte reacts must be small and the mercuric pool is reference electrode as anode . It is usually used for determination of the reduction side .

The plot of the applied potential versus corresponding current

is called polrogram .

The apparatus

is called a polarograph

The most important microelectrode for voltammetry and the used in early work, is the dropping mercury electrode (DME)

The dropping mercury electrode (DME).

A typical dropping mercury electrode is shown as part of the polarographic cell in Figure 1. Here, mercury is forced through a 5-to 10-cm capillary tubing with an internal diameter of approximately 0.05 mm . Under a head of about 50 cm of mercury, a continuous flow of identical droplets with diameters of 0.05 to 1 mm resultsthe lifetime of an individual drop is 2 to 6 seconds.

as shown in figure 1

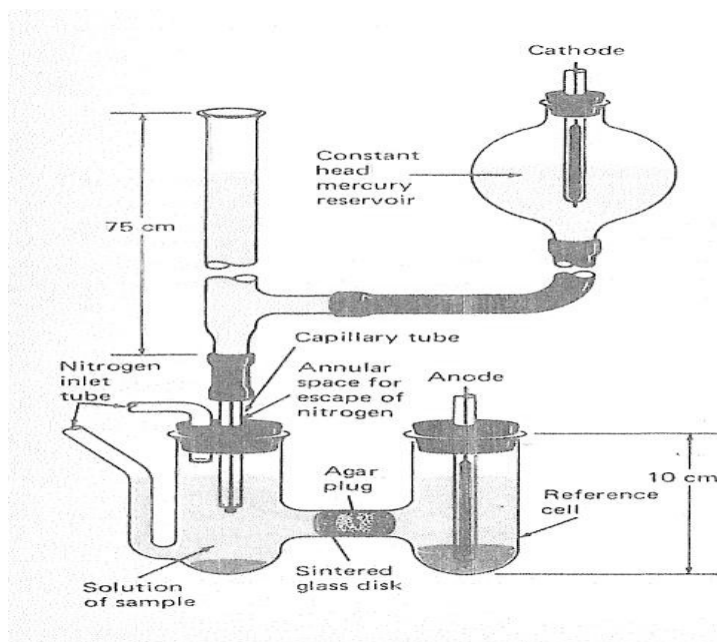


Figure 1 : A dropping mercury electrode and cell.(Polarograph)

The success of a polarographic experiment is critically dependent upon the reproducible behavior of the dropping electrode.

To prevent its becoming contaminated when not in use, the electrode should be rinsed thoroughly with water and dried.

When an external electromotive force (e.m.f) is applied to the cell that containing solution of substance that can be reduced e.g. CdCl_2 , the following reaction will occur



Polrograms

A polarogram is a plot of current as a function of the potential applied to a polarographic cell.

When the applied potential is zero, no current will flow through the cell By increasing the applied potential, current (due to reduction of the analyte) will not flow in the cell until its magnitude reaches a decomposition potential . Above the decomposition potential, reduction of the electro-active species is initiated and the observed current increases with increasing the potential . The current will continue to rise until it reaches a value called limiting current.

Further increase in applied potential does not produce any increase in the flowing current.

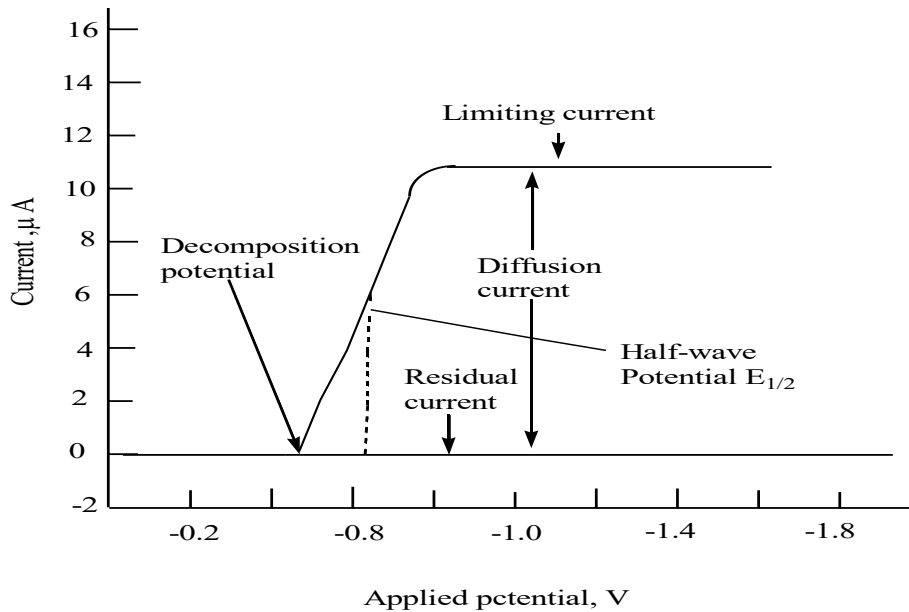
Although there is no reduction takes place below the decomposition potential, and hence no current is produced due to the reduction of the analyte, there is a small current still flow in the cell. The current is called residual current which is caused by the reduction of trace impurities in the sample solution or by migration of the ions of the supporting electrolyte

The polarogram is characterized by different parameters:

Residual current; at small applied potential only a residual current which caused by the reduction of trace impurities in the sample solution or by migration of the ions of the supporting electrolyte

Limiting current: is the region on the polarogram in which in which the current after increasing sharply, become essentially independent of the applied potential.

Diffusion current: it the difference between the limiting and residual current is directly proportional to the concentration of the reactive



A typical polarogram is shown in figure 2
 Figure 2: Polarogram for cadmium ion. The upper curve is for a solution that is $1 \times 10^{-3} \text{ M}$ with respect Cd^{2+} and 0.1 M with respect to KCl . The lower curve is for a solution that is 0.1 M in KCl only

- **Half-wave potential ($E_{1/2}$):** is the potential at which the current is equal to one-half the diffusion current. The half-wave potential is usually given the symbol $E_{1/2}$; it may permit qualitative identification of the reactant.
- **Decomposition potential:** is the potential at which the substance begin to oxidize or reduce.

Factors affecting the applicability and the accuracy of polarography.

- **Temperature control.** The diffusion currents for most substance are found to increase by about 2.5% per degree Celsius. Thus, solutions must be thermostated to a few tenths of a degree for accurate polarographic analysis.
- **Oxygen removal.** Oxygen removal is ordinarily the first step in a polarographic analysis. De aeration of the solution for several minutes with an inert gas accomplishes this end. A stream of the same gas, usually nitrogen, is passed over the surface during the analysis to prevent reabsorption.

3-Current maxima. Maxima are troublesome because they interfere with the accurate evaluation of diffusion currents and half-wave potentials. The cause or causes of maxima are not fully understood; fortunately, however, considerable empirical knowledge exists for their elimination. The addition of traces of such high-molecular-weight substances as gelatin, Triton X-100 (a commercial surface-active agent), methyl red, other dyes, or carpenter's glue is effective. The first two of these additives are particularly useful

- Diffusion current
- When the potential applied to a polarographic cell exceeds the decomposition potential of an electrolyte species. The resulting current flow is proportional to the rate of diffusion.
- The diffusion current is given by Ilkovic equation

$$I_d = 607 n D^{1/2} C m^{2/3} t^{1/6}$$

- I_d = is the average diffusion current in micro-ampere
- n = is the number of electrons consumed in the reduction of one molecule of electro-active species.
- D = diffusion coefficient of analyte , $\text{cm}^2 \text{s}^{-1}$
- C = concentration of analyte , mM
- M = is the rate of (mass) of flow of mercury from the dropping mercuric electrode expressed in mg/s
- t = drop life , s (drop time in s)

- **The constant 607 is a combination of natural constants including the Faraday's constant , it is slightly temperature – dependent and this value (607) at 25°C.**
 - **If the other parameters are kept constant, then the diffusion current will be dependent only on the analyte concentration then $I_d = KC$**
 - **The proportionality (direct) between the diffusion current and concentration of the substance is the basis of quantitative polarographic analysis.**
-
- **Determination of diffusion current.**
 - **For analytical work, limiting currents must always be corrected for the residual current. A residual current curve is ordinarily obtained immediately before or after acquiring the polarogram for the analyte. The diffusion current is taken as the difference between the two at some potential in the limiting current region (see Fig 2).**

- **Concentration determination.**
- **The best and most straight forward method for quantitative polarographic analysis involves**
 - 1- Calibration with a series of standard solutions (calibration curve). As nearly as possible, these standards should be identical with the samples being analyzed and cover a concentration range within which the unknown samples will likely fall. The linearity of the current-concentration relationship can be assessed from such data.**

2-The standard addition method.

is also applicable to polarographic analysis(The current is measured before and after addition of a small volume of a standard to a known volume of the sample). This procedure is particularly effective when the diffusion current is sensitive to other constituents that are present in the sample.

Advantages of the dropping mercury electrode.

The first is the large over voltage for the formation of hydrogen from hydrogen ions. As a consequence, the reduction of many substances from acidic solutions can be studied without interference.

Second, because a new metal surface is continuously generated, the behavior of the electrode is independent of its history. Thus, reproducible current-voltage curves are obtained regardless of how the electrode has been used previously.

The third useful feature is that reproducible average currents are immediately achieved at any given applied potential.

Disadvantages of the dropping mercury electrode: (limitation)

The first The most serious limitation to the dropping electrode is the ease with which mercury is oxidized; Thus, the dropping mercury electrode can be employed only for the analysis of reducible or very easily oxidizable substances.

Second, Other disadvantages are that it is slow to use and tends to malfunction by clogging (plugging).

Analytical Applications of Polarography;

1- Inorganic Polarographic Analysis

The polarographic method is generally applicable to the analysis of inorganic substances. Most metallic cations, for example, are reduced at the dropping electrode to form a metal amalgam or an ion of lower oxidation state. Even the alkali-and alkaline-earth metals are reducible, provided the supporting electrolyte used does not decompose at the high potentials required. The tetra alkyl ammonium halides serve this function well.

- **2. Organic Polarographic Analysis**
- **Organic compounds containing any of the following functional groups can be expected to react at the dropping mercury electrode and produce one or more polarographic waves.**
- **The carbonyl group includes aldehydes, ketones, and quinines. Aldehydes tend to be reduced at lower potentials than ketones. Conjugation of the carbonyl double bond also leads to lower half-wave potentials.**

2- Certain carboxylic acids are reduced polarographically, although the simple aliphatic and aromatic monocarboxylic acids are not. Dicarboxylic acids such as fumaric, maleic, or phthalic acid, in which the carboxyl groups are conjugated with one another, give characteristic polarograms. The same is true of certain keto and aldehydo acids.

3- Most peroxides and epoxides yield useful polarograms.

4- Nitro, nitroso, amine oxide, and azo groups are generally reduced at the dropping electrode.

5- Most organic halogen groups produce a polarographic wave as the halogen is replaced with an atom of hydrogen.

6- The carbon/carbon double bond is reduced when it is conjugated with another double bond, an aromatic ring, or an unsaturated group.

7- Hydroquinones and mercaptans produce anodic waves. In addition, numerous applications to biological systems have been reported.

Band group	Compound		Product
C = N	Ar-CH=CH-Ar	→	Ar-CH ₂ -CH ₂ -Ar
N = N	Ar-N=N-Ar	→	Ar-NH-NH-Ar
C = N	(Ar) ₂ -C=N-Alk	→	(Ar) ₂ -CH-NH-Alk
C = O	Ar-C=O-Alk	→	Ar-CH(OH)-Alk
O-O		→	2 OH-
S-S		→	2 SH-
C = N-		→	-CH-NH-
C-hal	R-CH ₂ -Br	→	-R-CH ₃ +Br
-NO ₂	Ar-NO ₂	→	Ar-NHOH

The following functional groups can be reduced at DME.

- One the easiest and most frequently organic reductions is that of the nitro group. In **nitrofurans** and **nitroimidazoles** for example, the reaction is.
- **Nitrofurantion**, **metronidazole** and **Tinidazole** are example whose reductions have been shown to follow this route.

- **Amperometric Titrations .**
- **The polarographic method can be used to estimate the equivalence point of a reaction, provided at least one of the products of the titration is oxidized or reduced at a microelectrode. Here, the current in a polarographic cell at some fixed potential is measured as a function of titrant volume . Plots of the data on either side of the equivalence point are straight lines with differing slopes; the end point can be fixed by extrapolation to their intersection .**

The amperometric method is more accurate than the polarographic method and less dependent upon the characteristics of the electrode and the supporting electrolyte. Furthermore, the temperature need not be fixed accurately, although it must be kept constant during the titration. Finally, the substance being determined need not be reactive at the electrode.

VOLTAMMETRY

Voltammetry is the technique which concerned with the study of voltage – current relationships during electrolysis in a cell, (Measurement of the current as a function of the applied potential)

Electrolysis : is the occurrence of chemical reaction under the influence of an electromotive force at electrode immersed in solution.

In voltammetry, the plot of the measured current as a function of applied potential is called voltammogram. Basic instrument for voltammetric measurements. (polarogram)

Electrochemical cell for voltammetric study composed of three electrodes

Working (indicator) electrode: is the electrode at which oxidation or reduction of the analyte takes place. Its surface area is small and it is completely polarized e.g. dropping mercuric electrode (DME), solid electrodes like gold, platinum and carbon.

Reference electrode: has a potential that remain constant during measurements this electrode is larger in size relative to working electrode and non polarized (depolarized) e.g. Saturated calomel electrode (SCE)

Counter electrode: is used to complete the electrical circuit . It made from gold or platinum.

Supporting electrolyte: Solution of electrolyte not oxidized or reduced (not react) with electrodes but has conductivity of the solution e.g. KNO_3

Polarization : Suppose an electrode (cathode) having a small surface area immersed in a solution (containing metal ions M^+) with a second large electrode and a voltage is applied across the two electrodes, the reaction $\text{M}^+ + \text{e} \longrightarrow \text{M}^\circ$ can take place at the small electrode

When the electrode has become polarized, a fresh supply of M^+ ions to its surface is controlled by the rate of mass transfer the metal ions from the bulk of the solution to the electrode surface .

- **Amperometric Titrations .**
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- **Plots of the data on either side of the equivalence point are straight lines with differing slopes; the end point can be fixed by extrapolation to their intersection**

The amperometric method is more accurate than the polarographic method and less dependent upon the characteristics of the electrode and the supporting electrolyte. Furthermore, the temperature need not be fixed accurately, although it must be kept constant during the titration. Finally, the substance being determined need not be reactive at the electrode.

Ch 27 Gravimetric Analysis

Analytical chemistry

Classification by the techniques:

1. Classical Analysis

Gravimetric, Titration(Volumetric) Analysis

2. Instrumental Analysis

Electrochemical Analysis,

Spectrochemical Analysis,

Chromatographic Separation and Analysis

Ch 12 Gravimetric Analysis

gravi – metric
(weighing - measure)

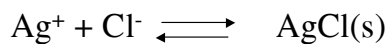
Definition: A **precipitation** or **volatilization** method based on the determination of weight of a substance of known composition that is chemically related to the **analyte**.

12.1 Procedure

Criteria

(1) The desired substance: completely precipitated.

"common ion" effect can be utilized:



excess of Cl^- which is added

(2) The weighed form: known composition.

(3) The product: "pure", easily filtered..

12. 1 Procedure

- 7 Steps in Gravimetric Analysis
 - 1) Dry and weigh sample
 - 2) Dissolve sample
 - 3) Add **precipitating reagent** in excess
 - 4) **Coagulate** precipitate usually by heating
 - 5) Filtration-separate precipitate from **mother liquor**
 - 6) Wash precipitate
 - 7) Dry and weigh to **constant weight** (0.2-0.3 mg)

Suction Filtration

- Filter flask
- Buchner funnel
- Filter paper
- Glass frit
- Filter adapter
- Heavy-walled rubber tubing
- Water aspirator



Suction Filtration

- Mother liquor



12.2

Advantages/Disadvantages

- Experimentally simple and elegant
- Accurate
- Precise (0.1-0.3 %)
- Macroscopic technique-requires at least 10 mg ppt to collect and weigh properly
- Time-consuming (1/2 day?)

12.3 Calculation

- Design of experiment
- Content Calculation
- Evaluation of the results

12.3 Calculation

- % of analyte, % A
- $\%A = \frac{\text{weight of analyte}}{\text{weight of sample}} \times 100$
- weight of ppt directly obtained $\rightarrow \%A$

How Do We Get %A?

- % A = $\frac{\text{weight of ppt} \times \text{gravimetric factor (G.F.)}}{\text{weight of sample}} \times 100$
- G.F. = $\frac{a \text{ FW[analyte]}}{b \text{ FW[precipitate]}}$
- G.F. = # gms of analyte per 1 gm ppt

The Gravimetric Factor

- G.F. = $\frac{a \text{ FW[analyte]}}{b \text{ FW[precipitate]}}$
- | <u>Analyte</u> | <u>ppt</u> | <u>G.F.</u> |
|--|----------------------------------|-------------|
| CaO | CaCO ₃ | |
| FeS | BaSO ₄ | |
| UO ₂ (NO ₃) ₂ ·6H ₂ O | U ₃ O ₈ | |
| Cr ₂ O ₃ | Ag ₂ CrO ₄ | |

Gravimetric Factor

<u>Analyte</u>	<u>ppt</u>	<u>G.F.</u>
CaO	CaCO ₃	CaO/CaCO ₃
FeS	BaSO ₄	FeS/BaSO ₄
UO ₂ (NO ₃) ₂	U ₃ O ₈	3UO ₂ (NO ₃) ₂ /U ₃ O ₈
Cr ₂ O ₃	Ag ₂ CrO ₄	Cr ₂ O ₃ /2Ag ₂ CrO ₄

Problem

- Consider a 1.0000 g sample containing 75% potassium sulfate (FW 174.25) and 25% MSO₄. The sample is dissolved and the sulfate is precipitated as BaSO₄ (FW 233.39). If the BaSO₄ ppt weighs 1.4900, what is the atomic weight of M²⁺ in MSO₄?
- ANS: Mg²⁺

Answer

- The hard part is setting up the correct equation

$$1.4900 = \frac{0.75 * 233.39}{174.25} + \frac{0.25 * 233.39}{x + 96.06}$$

- Rearranging and solving:

$$0.4855 = \frac{58.3475}{x + 96.06}; x = 24.12(\text{Mg}^{2+})$$

Problem

- A mixture of mercurous chloride (FW 472.09) and mercurous bromide (FW 560.99) weighs 2.00 g. The mixture is quantitatively reduced to mercury metal (At wt 200.59) which weighs 1.50 g. Calculate the % mercurous chloride and mercurous bromide in the original mixture.
- ANS: 0.5182 g

Answer

- Again, important to set up correct equation:

$$1.50 = \frac{2 * 200.59 * x}{472.09} + \frac{2 * 200.59(2 - x)}{560.99}$$

- Rearranging and solving:

$$0.8498 + 0.7151(2 - x) = 1.50$$

$$x = 0.5182g$$

- Example: How many mL of 1% potassium chloride would be needed to precipitate all of the silver in a 0.5 g ore sample that contains 1.5 parts per thousand silver? Allow for a 50% excess of the chloride solution.

12.4 Representative Gravimetric Analyses

Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
K ⁺	KB(C ₆ H ₅) ₄	KB(C ₆ H ₅) ₄	NH ₄ ⁺ , Ag ⁺ , Hg ²⁺ , TI ⁺ , Rb ⁺ , Cs ⁺
Mg ²⁺	Mg(NH ₄)PO ₄ ·6H ₂ O	Mg ₂ P ₂ O ₇	Many metals except Na ⁺ and K ⁺
Ca ²⁺	CaC ₂ O ₄ ·H ₂ O	CaCO ₃ or CaO	Many metals except Mg ²⁺ , Na ⁺ , K ⁺
Ba ²⁺	BaSO ₄	BaSO ₄	Na ⁺ , K ⁺ , Li ⁺ , Ca ²⁺ , Al ³⁺ , Cr ³⁺ , Fe ³⁺ , Sr ²⁺ , Pb ²⁺ , NO ₃ ⁻
Ti ⁴⁺	TiO(5,7-dibromo-8-hydroxyquinoline) ₂	Same	Fe ³⁺ , Zr ⁴⁺ , Cu ²⁺ , C ₂ O ₄ ²⁻ , citrate, HF
VO ₃ ⁻	Hg ₂ VO ₄	V ₂ O ₅	Cl ⁻ , Br ⁻ , I ⁻ , SO ₄ ²⁻ , CrO ₄ ²⁻ , AsO ₄ ³⁻ , PO ₄ ³⁻
Ce ³⁺	PbCrO ₄	PbCrO ₄	Ag ⁺ , NH ₄ ⁺
Mn ²⁺	Mn(NH ₄)PO ₄ ·H ₂ O	Mn ₂ P ₂ O ₇	Many metals
Fe ³⁺	Fe(HCO ₃) ₃	Fe ₂ O ₃	Many metals
Co ²⁺	Co(1-nitroso-2-naphtholate) ₂	CoSO ₄ (by reaction with H ₂ SO ₄)	Fe ³⁺ , Pd ²⁺ , Zr ⁴⁺

Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
Ni ²⁺	Ni(dimethylglyoximate) ₂	Same	Pd ²⁺ , Pt ²⁺ , Bi ³⁺ , Au ³⁺
Cu ²⁺	CuSCN	CuSCN	NH ₄ ⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺
Zn ²⁺	Zn(NH ₄)PO ₄ ·H ₂ O	Zn ₂ P ₂ O ₇	Many metals
Ce ⁴⁺	Ce(IO ₃) ₄	CeO ₂	Th ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺
Al ³⁺	Al(8-hydroxyquinolate) ₃	Same	Many metals
Sn ⁴⁺	Sn(cupferron) ₂	SnO ₂	Cu ²⁺ , Pb ²⁺ , As(III)
Pb ²⁺	PbSO ₄	PbSO ₄	Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Hg ²⁺ , Ag ⁺ , HCl, HNO ₃
NH ₄ ⁺	NH ₄ B(C ₆ H ₅) ₄	NH ₄ B(C ₆ H ₅) ₄	K ⁺ , Rb ⁺ , Cs ⁺
Cl ⁻	AgCl	AgCl	Br ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
Br ⁻	AgBr	AgBr	Cl ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
I ⁻	AgI	AgI	Cl ⁻ , Br ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
SCN ⁻	CuSCN	CuSCN	NH ₄ ⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺
CN ⁻	AgCN	AgCN	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻
F ⁻	(C ₆ H ₅) ₃ SnF	(C ₆ H ₅) ₃ SnF	Many metals (except alkali metals), SiO ₄ ⁴⁻ , CO ₃ ²⁻
ClO ₄ ⁻	KClO ₄	KClO ₄	
SO ₄ ²⁻	BaSO ₄	BaSO ₄	Na ⁺ , K ⁺ , Li ⁺ , Ca ²⁺ , Al ³⁺ , Cr ³⁺ , Fe ³⁺ , Sr ²⁺ , Pb ²⁺ , NO ₃ ⁻
PO ₄ ³⁻	Mg(NH ₄)PO ₄ ·6H ₂ O	Mg ₂ P ₂ O ₇	Many metals except Na ⁺ , K ⁺
NO ₃ ⁻	Nitron nitrate	Nitron nitrate	ClO ₄ ⁻ , I ⁻ , SCN ⁻ , CrO ₄ ²⁻ , ClO ₃ ⁻ , NO ₂ ⁻ , Br ⁻ , C ₂ O ₄ ²⁻
CO ₃ ²⁻	CO ₂ (by acidification)	CO ₂	(The liberated CO ₂ is trapped with Ascarite and weighed.)

Table 27-2 Common organic precipitating agents		
Name	Structure	Ions precipitated
Dimethylglyoxime		Ni ²⁺ , Pd ²⁺ , Pt ²⁺
Cupferron		Fe ³⁺ , VO ₂ ⁺ , Ti ³⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Ga ³⁺ , Sn ⁴⁺
8-Hydroxyquinoline (oxine)		Mg ²⁺ , Zn ²⁺ , Cu ²⁺ , Cd ²⁺ , Pb ²⁺ , Al ³⁺ , Fe ³⁺ , Bi ³⁺ , Ga ³⁺ , Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺ , TiO ₂ ²⁺
Salicylaldoxime		Cu ²⁺ , Pb ²⁺ , Bi ³⁺ , Zn ²⁺ , Ni ²⁺ , Pd ²⁺
1-Nitroso-2-naphthol		Co ²⁺ , Fe ³⁺ , Pd ²⁺ , Zr ⁴⁺
Nitron		NO ₃ ⁻ , ClO ₄ ⁻ , BF ₄ ⁻ , WO ₄ ²⁻
Sodium tetraphenylborate	Na ⁺ B(C ₆ H ₅) ₄ ⁻	K ⁺ , Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Ag ⁺ , organic ammonium ions
Tetraphenylarsonium chloride	(C ₆ H ₅) ₄ As ⁺ Cl ⁻	Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , ReO ₄ ⁻ , MoO ₄ ²⁻ , WO ₄ ²⁻ , ClO ₄ ⁻ , I ₃ ⁻

12.5 The Precipitation Process

1. Particle Size / Filterability

- produce particles large enough to be 'caught'
- ideally, produce crystals
- avoid colloidal suspension

Particle size and filterability

Colloidal Suspensions

Size range: 10^{-6} - 10^{-4} mm

No tendency to settle

Difficult or impossible to filter

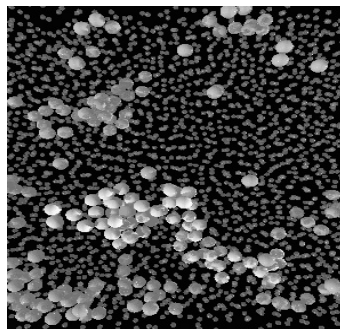
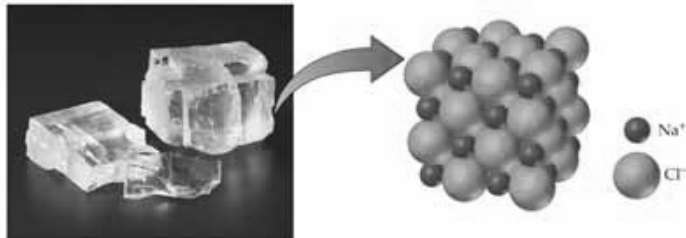
Crystalline suspensions

Size Range: 10^1 - 10 mm

Will settle spontaneously

Readily filtered

Typically of higher purity than colloids



2. Mechanism of Precipitation

Crystal Forming:

nucleation

particle growth

Mechanisms of precipitation

Two competing processes

Nucleation

When a small number of ions, atoms, molecules initially unite.

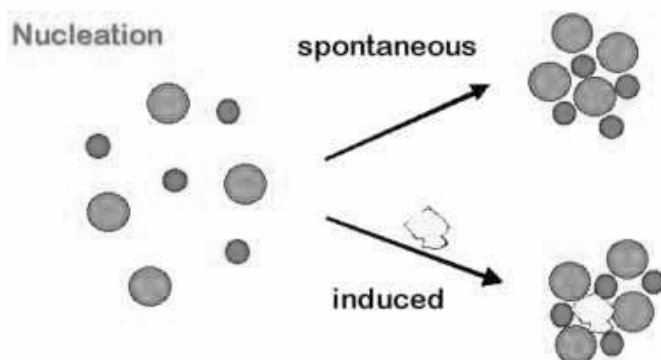
Spontaneous

Induced

Particle growth

The three dimensional growth of a particle nucleus into a larger crystal.

Mechanisms of precipitation



Spontaneous nucleation will occur on its own.

Induced nucleation requires a 'seed' particle to get things started (dust, another crystal, glass fragment, ...)

Mechanisms of precipitation

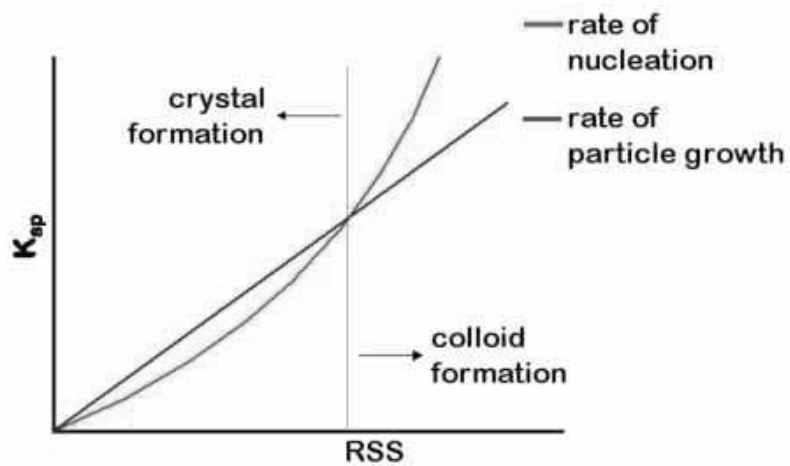
Particle growth



Once a nucleation site has formed, other ions are attracted to the site. This will result in the formation of large, filterable particles.

If done properly, it also reduces contaminants since they don't 'fit in' to the crystal structure.

Mechanisms of precipitation



Partide size and filterability

We have some control on particle size based on how we add our reagents.

Relative supersaturation (RSS)

$$RSS = \frac{Q - S}{Q}$$

Where

Q = concentration of solute at any time

S = equilibrium solubility of solute

RSS can be used estimate/control the type of precipitate that is formed.

Mechanisms of precipitation

Rate of nucleation is $\propto e^{-Q/RT}$ RSS

Rate of particle formation is $\propto Q^{-1}$ RSS

If RSS is large, nucleation is favored and colloidal suspensions tend to be formed.

If RSS is small, particle growth will predominate resulting in crystalline precipitates.

Mechanisms of precipitation

The goal is to form crystalline precipitates so RSS must be minimized.

This can be done by:

Increasing S

Elevate temperature, pH control

Decrease Q

Use dilute solutions

Slowly add reagents

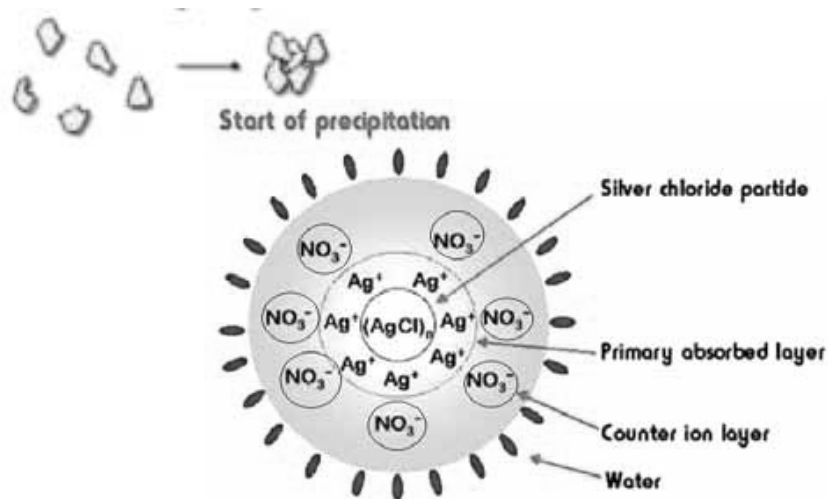
Stirring the solution

Techniques to promote crystal growth

- (1). Raising the temperature to increase S and thereby decrease relative supersaturation.
- (2). Adding precipitant slowly with vigorous mixing, to avoid a local, highly supersaturated condition where the stream of precipitant first enters the analyte.
- (3). Keeping the volume of solution large so that the concentration of analyte and precipitant are low.

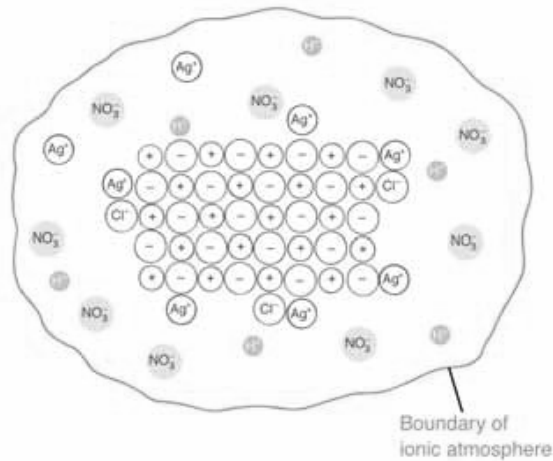
3. Other ways to obtain a good precipitate

- (1) Increasing the electrolyte concentration



High Electrolyte Concentration to Aid Precipitation

- (1) Decreasing the volume of the counter-ion layer
- (2) Increasing the chance for coagulation



3. Other ways to obtain a good precipitate

- (2) Using a volatile electrolyte

AgCl, wash with HCl. Drying precipitate at 110°C will remove HCl.

This displaces the less volatile, excess counter ion.

Treatment of colloidal precipitates

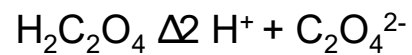
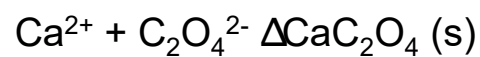
(3) Digestion and aging

Digestion. Heating the solution for about an hour after precipitate formation. This helps to remove weakly bound water.

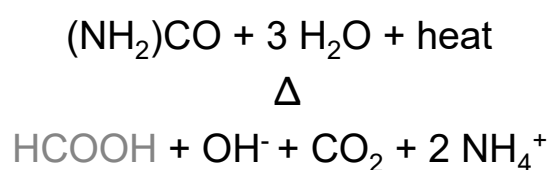
Aging. Storing the solution, unheated, overnight. This allows trapped contaminants time to 'work their way out.'

Both can result in a denser precipitate that is easier to filter.

(4) pH control of precipitation



(5) Homogeneous Precipitation



Exercises

1. To obtain a precipitate which is useful for gravimetric analysis, the analyst tries to obtain conditions to encourage crystal growth, as opposed to the formation of a colloid. Which of the following statements aids in the formation of a crystalline precipitate?

- (a) The solution is kept cool to slow down the movement of ions to allow crystals to form.
- (b) The solutions are made as dilute as practical to allow crystals to form slowly.
- (c) The solutions are mixed rapidly to allow the appropriate ions to make contact without interference of other materials.

Exercises

2. Which of the following processes is true regarding the digestion of a solution containing a precipitate?

- (a) Digestion tends to increase particle size of the precipitate.
- (b) Digestion is used to slow down the coagulation of a colloidal precipitate because of the increased energy added to the solution.
- (c) A long digestion is not recommended because the higher temperatures enable impurities to become trapped in the crystal lattice of the precipitate

Exercises

3. In the gravimetric analysis of iron, hydroxide may be added to a solution containing Fe^{3+} to precipitate a gelatinous mess which is ignited to form Fe_2O_3 . If 0.2864 grams of Fe_2O_3 were formed from the ignition of the precipitated mess, how many grams of FeCO_3 were contained in the original sample analyzed?

- (a) 0.4155 g FeCO_3
- (b) The answer cannot be computed because the sample did not contain any Fe^{2+} .
- (c) 0.2078 g FeCO_3

Exercises

4 A sample of ore containing manganese weighed 1.2354 grams. This sample was heated in a solution of nitric acid, which dissolved the manganese ion producing manganese(III) nitrate ($\text{Mn}(\text{NO}_3)_3$). The acidity of the solution was adjusted, and Hydrogen sulfide gas was bubbled into the solution producing 0.2876 grams of manganese(III) sulfide (Mn_2S_3). What is the percentage of manganese in the original sample?

- (a) 12.37% Mn
- (b) 6.19% Mn
- (c) 3.09% Mn

Exercises

5 Why do you reheat/recool the solid unknown until its weight stabilizes?

- a. To increase the precision of your measurement.
- b. To increase the accuracy of your measurement.
- c. To ensure that there is no water in your solid.
- d. To convert any nickel metal to nickel oxide.

Exercises

6 In Gravimetric Determination of Nickel, heating gently during the coagulation stage would aid what process?

- a. Precipitation -- more Nickel diglyme would come out of solution.
- b. Digestion -- particle size and purity increases due to recrystallization.
- c. Evaporation -- the solution becomes more concentrated so more precipitation occurs and filtering is easier.
- d. Calculation -- the waiting gives you time to work example problems and ask questions.

Exercises

7. A certain barium halide exists as the hydrated salt $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 cm³) and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.

Exercises

8. Summarize the conditions to improve an analytical precipitation in Gravimetric analysis.

Faculty of Pharmacy
Department of Pharmaceutical Analytical Chemistry



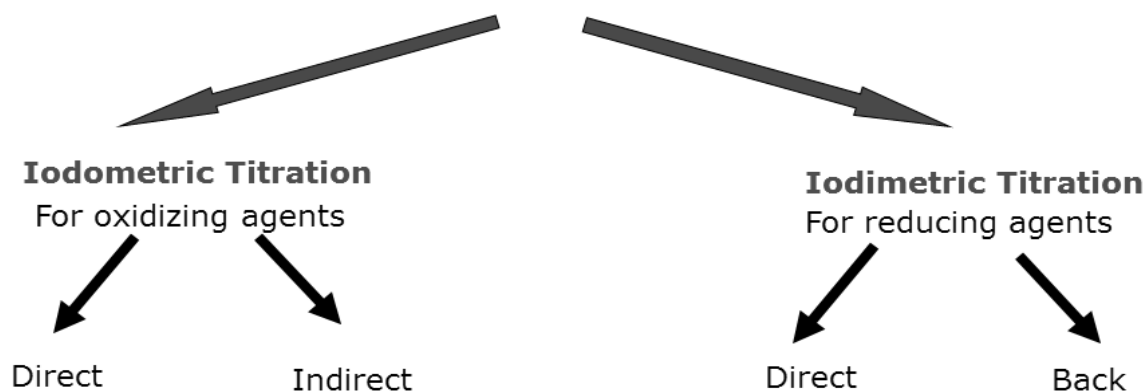
PRACTICAL PHARMACEUTICAL ANALYTICAL CHEMISTRY

DR. HYTHAM M. A. AHMED

Redox Titration

Redox titrations involving Iodine

Iodine is a weak oxidizing agent. It is a secondary standard substance as it is volatile



1- Iodimetric Titration

It is used for the determination of reductants

It may be direct or back titration.

1.1. Direct Iodimetry

Sample is directly titrated with Std. I_2 solution using starch or CCl_4 as indicator which is added from the beginning of the titration.

Color change

if using starch colorless \rightarrow Blue (in the aqueous layer)

if using CCl_4 colorless \rightarrow Pink (in the organic layer)

Examples

Determination of $Na_2S_2O_3$ sample.

1.2. Back Iodimetry

It is used when the reaction between the sample and I_2 is slow one.

Sample + measured Xss Std. I_2 → xss unreacted I_2 is then titrated against std. $Na_2S_2O_3$ using starch or CCl_4 as indicator.

Color change

if using starch Blue → colorless (in the aqueous layer)

if using CCl_4 Pink → colorless (in the organic layer)

Examples

Determination of Glucose.

2- Iodometric Titration

It is used for the determination of oxidants.

It may be direct or indirect titration.

2.2. Direct Iodometry :

Sample + KI → Equivalent amount of I_2 # std. $Na_2S_2O_3$ using starch or CCl_4 as indicator

Color change:

if using starch Blue → colorless (in the aqueous layer)

if using CCl_4 Pink → colorless (in the organic layer)

Example

Determination of $CuSO_4$

Indicators used

1- Starch

- It produces a dark blue complex with I_2 .
- It should be added near the E.P. (straw yellow) to prevent the formation of irreversible complex between I_2 and starch when the conc. of I_2 is high.
- It cannot be used in strongly acidic medium as it undergoes hydrolysis and in such case, we use organic solvent as indicator.

2- Organic Solvent

Examples: CCl_4 and $CHCl_3$

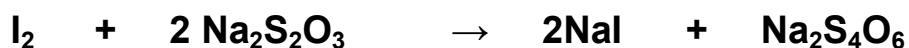
- They are immiscible and heavier than water.
- I_2 dissolves in the organic layer giving a pink color
- At the E.P., the color change would be (Pink \rightarrow colorless in the organic layer).

1. Determination of Sodium thiosulphate

IODIMETRIC METHOD

Principle

It is a reducing agent and can be directly titrated with standard iodine solution.



Procedure

- 1- Pipette 10 ml sample into a conical flask..
- 2- Add 2 ml starch.
- 3- Titrate with 0.05 M I₂ solution.

Color change

Colorless → Blue

Results:

<u>NO.</u>	<u>V1</u>	<u>V2</u>
<u>1</u>		
<u>2</u>		
<u>3</u>		
<u>Average</u>		

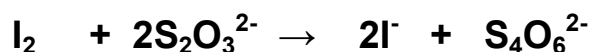
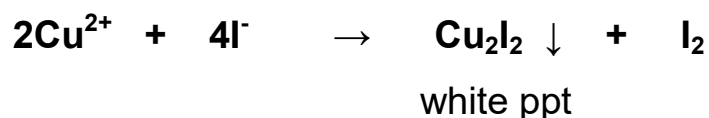
Calculation:

2. Determination of CuSO₄

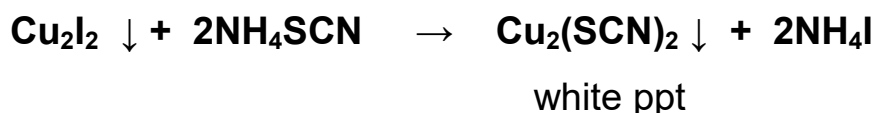
IODOMETRIC METHOD

Principle

Cupric salts reduced by iodide in a weakly acidic solution (PH 4-5) to cuprous iodide with the liberation of iodine which is titrated with standard thiosulphate solution according to the following reactions:



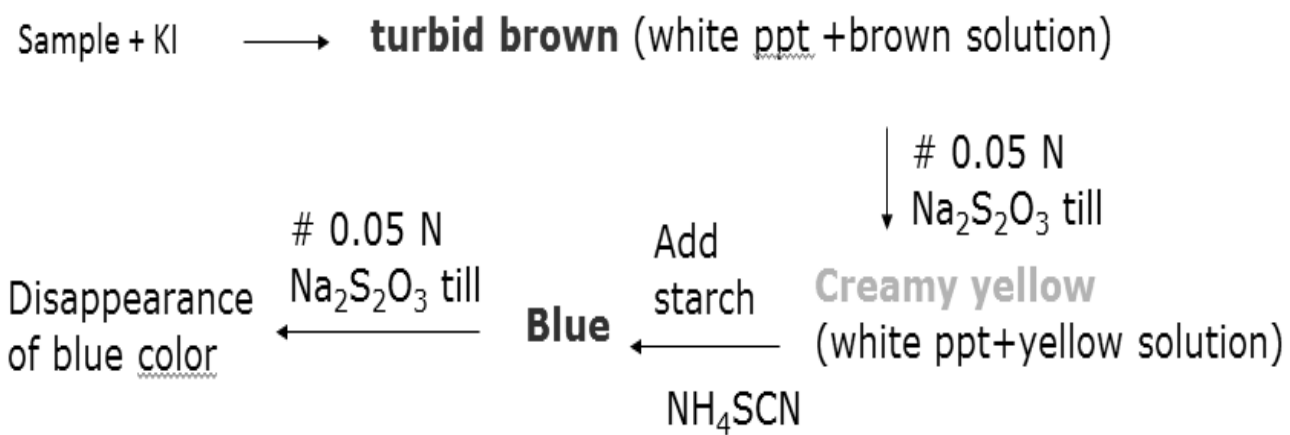
The cuprous iodide ppt adsorbs iodine giving a false premature E.P. so ammonium thiocyanate is added near the E.P. to form cuprous thiocyanate and set free the adsorbed iodine.



Procedure

- 1- Pipette 10 ml sample into a stoppered conical flask.
- 2- Add 10 ml KI solution.
- 3- Titrate # 0.05 M Na₂S₂O₃ till straw yellow then add 5 ml starch, 3 ml NH₄SCN and continue titration with dropwise addition and vigorous shaking till the disappearance of the blue color

Color change



Results:

<u>NO.</u>	<u>V1</u>	<u>V2</u>
<u>1</u>		
<u>2</u>		
<u>3</u>		
<u>Average</u>		

Calculation:

3. Potassium Iodate (KIO₃) As a Titrant **(Andrew's Method)**

- Potassium iodate is a strong oxidizing agent.
- It is a primary standard substance.

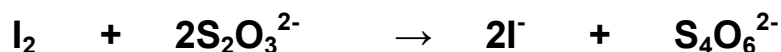
Determination of weak iodine solution

Principle

It is a solution of I₂ and KI in 85% alcohol.

For free I₂ Content

It is determined by direct titration with 0.05 N Na₂S₂O₃



For total I₂ + KI (Andrew's Method)

Titration : M/20 KIO₃.

Medium : Strong acidic medium(Conc. HCl) to stabilize the formed I⁺ in the form of ICl (iodonium monochloride).

Indicator: CCl₄ or CHCl₃ (starch cannot be used due to strong acidic medium).



Procedure

For I₂ content

- 1- Pipette 10 ml sample.
- 2- Titrate with 0.05 N Na₂S₂O₃ till straw yellow, then add 3ml starch and continue titration drop wise with vigorous shaking till the disappearance of the blue color.

Color change:

Blue → colorless (in the aqueous layer) e.p.1

For total content

- 1- Pipette another 10 ml sample into a stoppered conical flask
- 2- Add 10 ml conc.HCl.
- 3- Titrate with M/20 KIO₃ till pale brown color then add 3 ml CCl₄ and continue titration with vigorous shaking till CCl₄ layer becomes colorless.

Color change:

Pink → colorless (in the organic layer) e.p.2

Results:

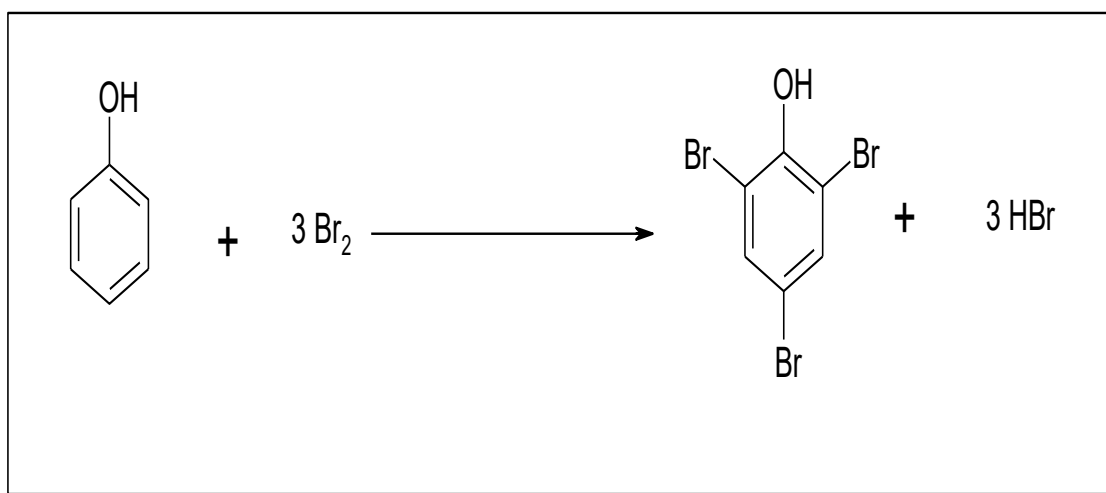
<u>NO.</u>	<u>V1</u>	<u>V2</u>
<u>1</u>		
<u>2</u>		
<u>3</u>		
<u>Average</u>		

Calculation:

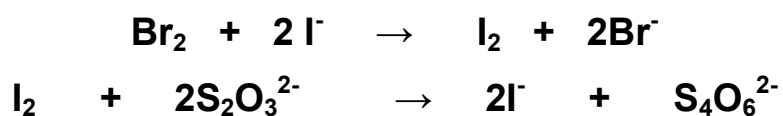
4. Phenol analysis

Principle

The determination depends on the reaction between phenol and bromine where phenol undergoes bromination by substitution of three hydrogen atoms on the benzene ring by bromine atoms.

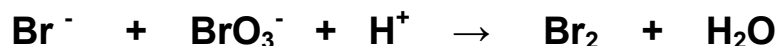


Since substitution reactions are slow, back titration procedure must be employed, thus a measured excess of standard bromine solution is added to phenol, the excess unreacted bromine is determined iodometrically.



Procedure

- 1- Pipette 10 ml sample into a stoppered conical flask.
- 2- Add 10 ml standard 0.05 N Br₂ (KBr/KBrO₃)
- 3- Add 5 ml conc.HCl (to liberate Br₂ from the mixture acc. to the following reaction:



- 4- Moist the stopper with KI solution and stopper the flask, leave for 15 min. in the dark* with shaking at intervals to ensure complete bromination.
- 5- Add 10 ml KI solution and shake well.
- 6- Titrate the liberated I₂ with 0.05 N Na₂S₂O₃ till straw yellow color then add 3 ml CCl₄* and 2 ml starch.
- 7- Continue titration with vigorous shaking till the aqueous and organic layers are colorless.

Color change:

In the aqueous layer : Blue → Colorless

In the organic layer : Pink → Colorless

* The reaction should be performed in the dark to prevent photo-oxidation of phenol and to prevent the addition reaction on the benzene ring of phenol.

* Tribromophenol is a viscous ppt which traps some of I₂ leading to a false premature E.P. so CCl₄ is added to dissolve it.

Results:

<u>NO.</u>	<u>V1</u>	<u>V2</u>
<u>1</u>		
<u>2</u>		
<u>3</u>		
<u>Average</u>		

Calculation:

Conductometric titration

In conductometric titrations, we detect the end point by following the change in the conductance of solution upon addition of titrant

Conductometric titration of HCl # 0.1N NaOH

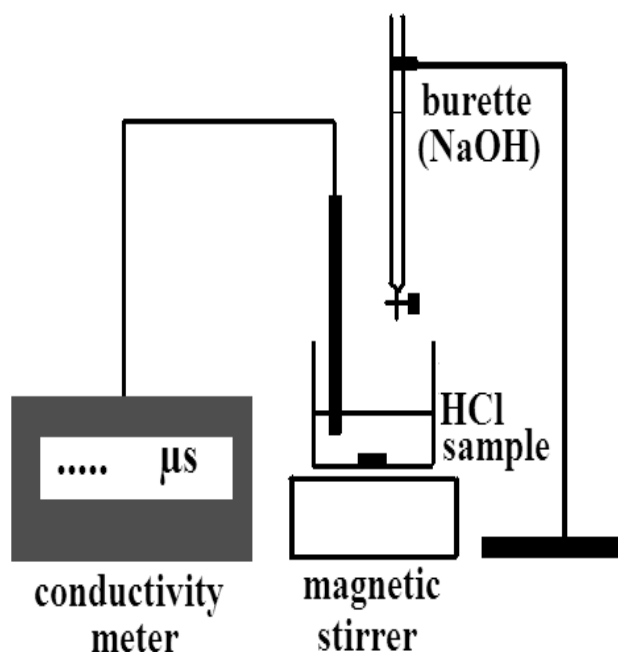
Procedure

1- Pipette 10 ml HCl sample into a 250 ml beaker and mix with 140 ml of dist water.

2- Immerse the electrode into the solution and measure the conductance in μs (ml titrant=0).

3- Titrate against 0.1 M NaOH (added at 2 ml intervals) and record the observed conductance.

4- Record the measured conductance in the provided table



<i>ml titrant</i>	<i>Measured Conductance (μs)</i>	<i>Corrected conductance (μs)</i> <i>=Meas.cond*(V_a+V_t)/V_a</i>
0		
2		
4		
6		
8		
10		
12		
14		

5- Calculate the corrected conductance

(the measured conductance must be corrected for the dilution due to addition of the titrant)

$$\text{Corrected} = \text{measured} * \frac{V_{\text{sample}} (150 \text{ ml}) + V_{\text{added titrant}} (0,2,4, \dots \text{ ml})}{V_{\text{sample}}(150 \text{ ml})}$$

6- Construct the conductometric titration curve. It is a relation between the conductance and the added volume of titrant in ml

Potentiometric titration

In potentiometric titrations, we detect the end point by following the change in the potential (measured in mV or pH) of solution upon addition of titrant.

Determination of pKa of acetic acid

Procedure

1- Pipette 10 ml acetic acid sample into a 250 ml beaker and mix with 140 ml of dist water using magnetic stirrer.

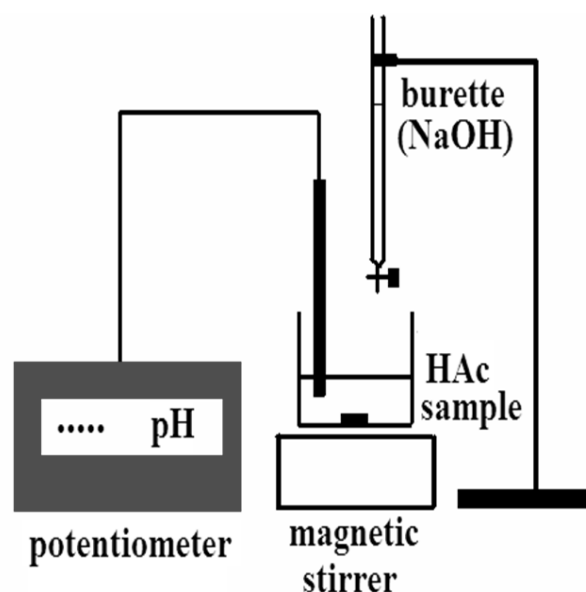
2- Immerse the electrode into the solution and measure the pH (ml titrant=0).

3- Titrate against 1 M NaOH (added at 0.5 ml intervals) and record the pH after each addition

4- Record the measured pH values in the provided table

5- Locate the end point using Titration curve

6- Determine the pKa from the allocated end point.



<i>ml titrant</i>	<i>pH</i>
0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	

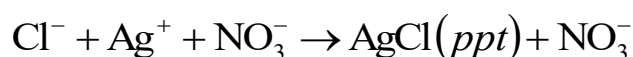
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Electrochemistry

Conductometry

To measure the conductance of a solution; conductance cell, conductometer, and a stirrer are needed. The cell is formed of two fixed platinum electrodes, the distance between them is constant; thus the distance between the two electrodes (L)/area of the electrode (A) is a constant value known as cell constant, which is stated on the cell. The conductometer gives conductivity reading in mS/cm or $\mu\text{S/cm}$.

Principle:

For the determination of chloride content of a water sample, conductometric titration with standard 0.05 N AgNO_3 is carried out and the reaction is represented by the following equation:



The initial conductivity will be due to the Cl^- with $76 \text{ Sm}^2/\text{mol}$ mobility, upon titration the Cl^- is replaced by NO_3^- with $71 \text{ Sm}^2/\text{mol}$ mobility, and then a continuous slight decrease in conductivity will be observed till the endpoint. Beyond the endpoint continuous high increase in conductivity occurs due to the addition of AgNO_3 titrant, which supplies the solution with Ag^+ of $64 \text{ Sm}^2/\text{mol}$ mobility, and NO_3^- of $71 \text{ Sm}^2/\text{mol}$ mobility. The titration curve thus becomes a two-armed curve. The point of intersection is the endpoint.

Procedure:

1. Using a pipette, transfer 10 mL of water sample in a 150 mL beaker.
2. Add distilled water to about half of the beaker.
3. Immerse the conductance cell, and the temperature probe in the sample. Place the beaker on the magnetic stirrer.
4. Measure the conductivity (K).
5. Titrate the sample by successive addition of 2 mL of standard 0.05 N AgNO_3 . Record the reading after each addition.
6. Continue titration for further 6 mL after the end point; shown by the abrupt increase in conductivity.
7. Plot a curve representing the conductivity readings versus the volume (mL) of titrant and locate the end point.

Calculations:

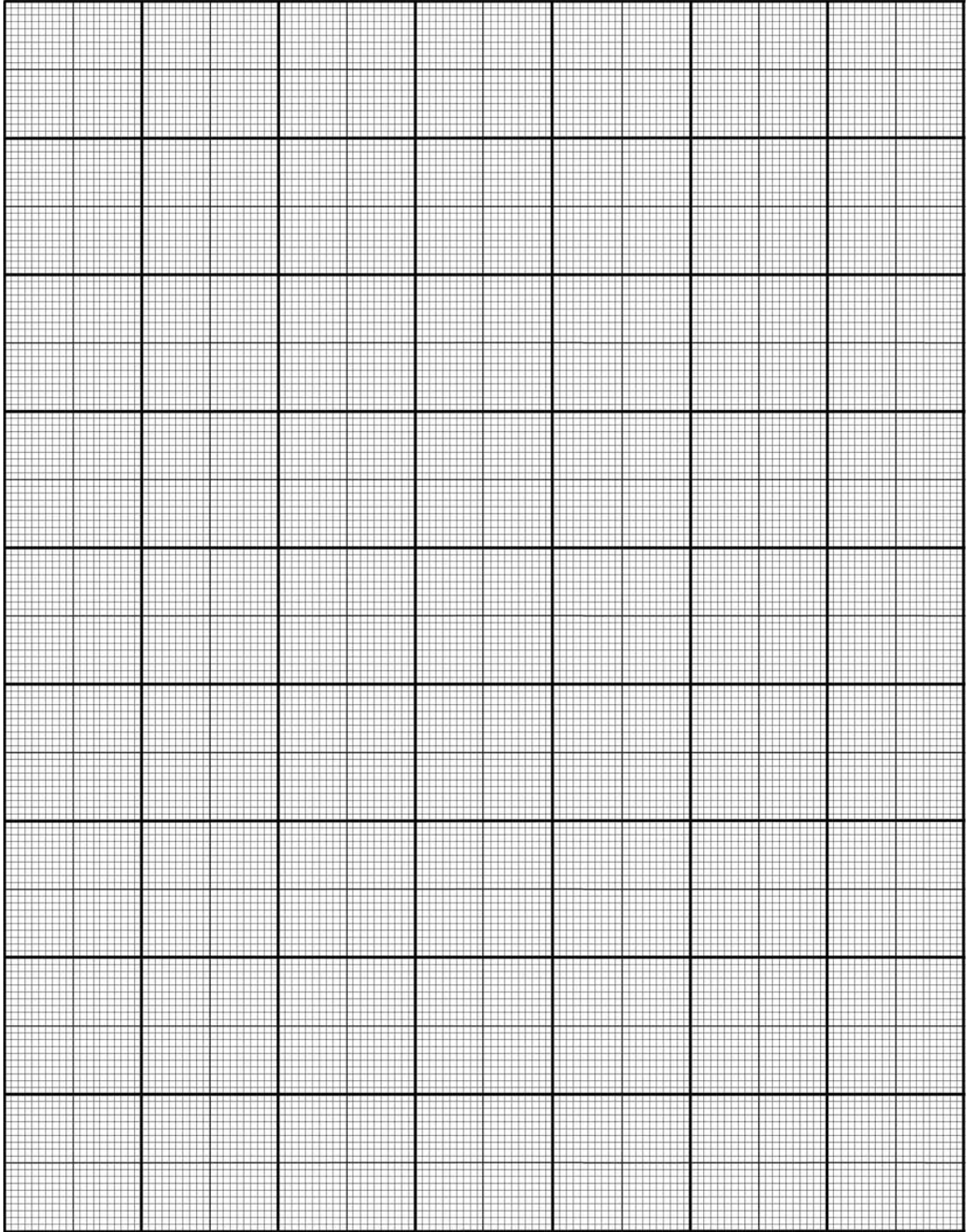
Volume (mL)	Conductivity (K)
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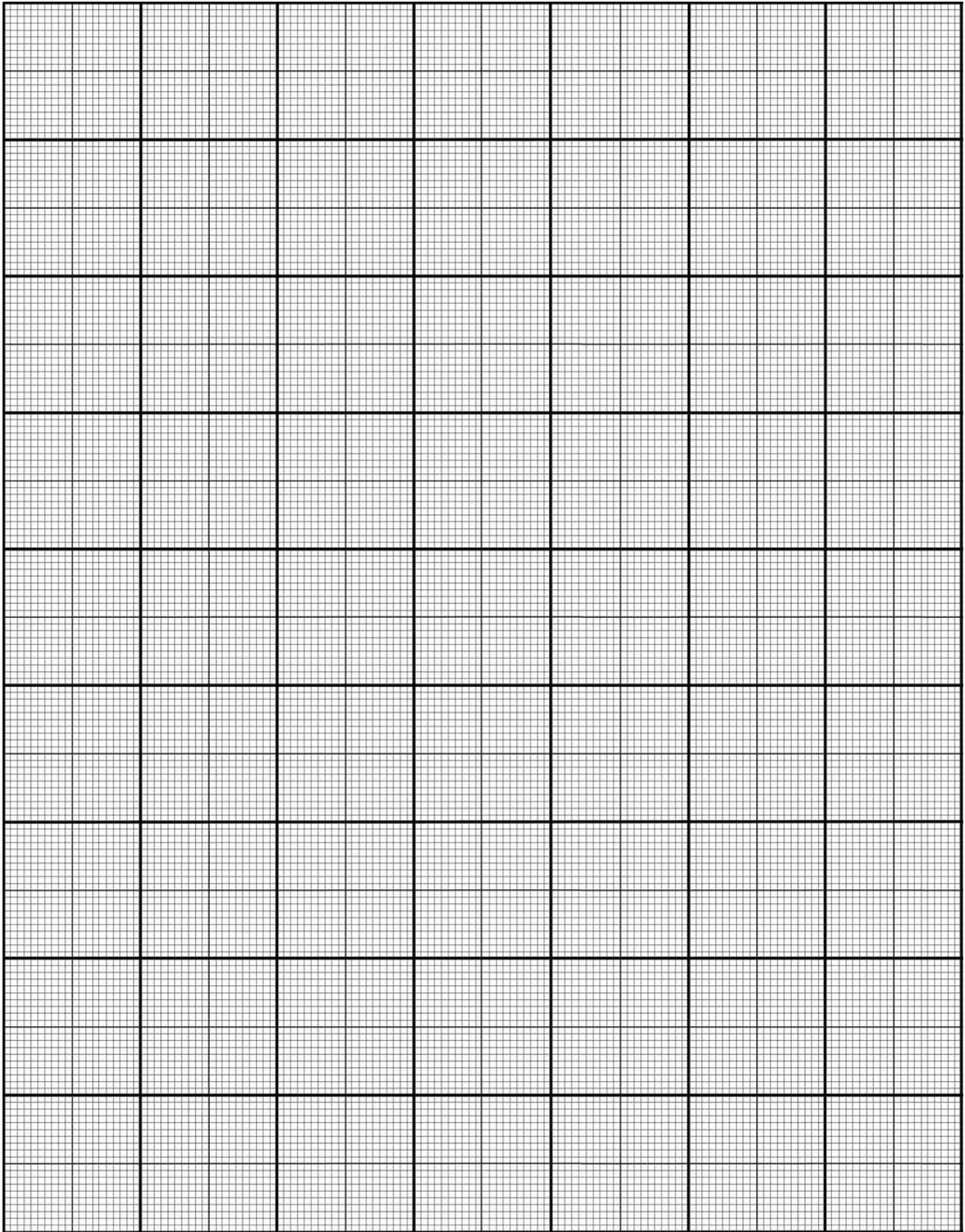
$\therefore 1 \text{ mL } 0.05 \text{ N AgNO}_3 \equiv 0.0000035 \mu\text{g of Cl}^- = F.$

$\therefore \text{Concentration of Cl}^- = \frac{\text{Endpoint} \times f \times F \times 1000}{\text{Sample volume}} = \dots\dots\dots \text{ppm.}$

Date:

Experiment:





Potentiometry

Direct Potentiometry

Determination of Unknown pH

Principle:

To measure the pH of a given solution, you need a glass-saturated reference calomel electrode system and a pH-meter (a potentiometer whose scale is calibrated to read pH directly).

Procedure:

1. You are provided with standard buffer solutions of pH values 4 and 7. Start pH calibration as follows:
 - a) Switch on the instrument and allow it to warm up for 5 minutes.
 - b) Rinse the electrode in distilled water.
 - c) Immerse the electrode together with the temperature probe in the standard buffer solution of pH = 4 and wait till a curve appears on the display then press CAL.
 - d) Remove the buffer solution; wash with distilled water, then calibrate the electrode response using buffer of pH = 7, as previously.
2. Rinse the electrode assembly in distilled water.
3. Immerse the electrode assembly in the solution of unknown pH and record the pH value.
4. Remove the electrode assembly and rinse in distilled water.
5. Store the electrodes while suspended in buffer solution of pH = 4 saturated with KCl.

Determination of pKa of a Weak Acid

Principle:

The pKa of a weak acid (such as acetic acid) can be calculated from the following formula:

$$\text{pH} = \frac{1}{2} \text{pKa} + \frac{1}{2} \text{pCa}$$

Accordingly, by measuring the pH of a weak acid solution of known concentration, its pKa can be calculated.

Procedure:

1. Prepare a series of acetic acid solutions of 0.1 N, 0.01 N and 0.001 N.
2. Calibrate the pH-meter.
3. Measure the pH of each of the prepared dilutions. Record your readings.
4. Apply the above formula for the determination of pKa.

Calculations:

Acetic acid concentration	pH	pKa	Average pKa
0.1 N
0.01 N	
0.001 N	

Date:

Experiment:

Indirect Potentiometry

Potentiometric titrations

Principle:

The potential is measured continuously after successive addition of the titrant. The obtained potential values are plotted versus the volume of titrant. The end point is revealed by sudden change of the potential. Three methods are used for the detection of the end point.

- a) By accurate location of the midpoint of the titration curve inflexion. This is carried out by extrapolation of the two horizontal arms of the curve; draw a perpendicular line, which crosses the inflexion. The point of intersection where the two halves of the line are equal is the end point.
- b) The second method is the first derivative method where a plot of the rate of change of potential per volume ($\Delta E/\Delta V$) versus volume is drawn. The end point is the maximum of the curve, which corresponds to the inflexion in the titration curve.
- c) The third method is the second derivative method, where a plot of the change of the rate of change of potential per volume ($\Delta^2 E/\Delta V^2$) versus volume is drawn so it becomes zero at the inflexion point and it provides a more exact measure of the end point, which is the intersection of the line joining the maximum and the minimum points of the curve.

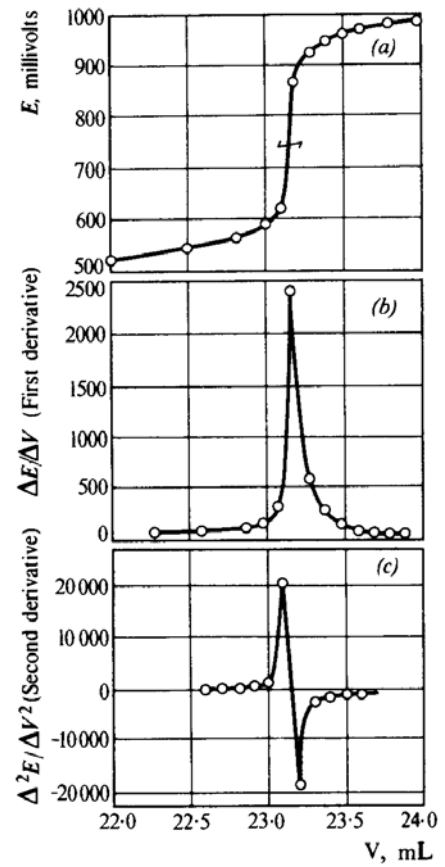
Procedure:

1. Calibrate the pH-meter as mentioned before.
2. Change the mode of operation to mV to measure the EMF of the cell.
3. In a 150 mL beaker, add 10 mL of the sample using 10 mL one mark pipette. Adjust volume to about 75 mL using distilled water.
4. Place the electrode assembly and a small magnet in the beaker, and then place it on a magnetic stirrer.
5. Fill the burette with standard 0.1 N NaOH and clamp the burette.
6. Allow magnet to stir the solution gently.
7. Add 2 mL of titrant; wait till a curve appears on the pH-meter display, which indicates a final reading.
8. Repeat addition of titrant 2 mL portion wise, and record the reading after each addition.
9. Observe the changes in potential readings, and when the difference starts to increase, add the titrant in portions of 1 mL.
10. When differences in readings start to decrease again, continue the addition of titrant in portions of 2 mL for two more times.
11. Tabulate your results.
12. Plot the titration curves by the three mentioned methods and locate the end point.
13. Calculate the concentration of HCl in the sample.

Calculations:

V (mL)	E (mV)	V'	$\Delta E/\Delta V$	V''	$\Delta^2 E/\Delta V^2$
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- End point of zero order = mL
- End point of first derivative = mL
- End point of second derivative = mL



$\therefore 1 \text{ mL } 0.1 \text{ N NaOH} \equiv 0.00365 \text{ g of HCl} = F.$

$$\therefore \text{Concentration of HCl} = \frac{\text{Endpoint} \times f \times F \times 1000}{\text{Sample volume}} = \dots\dots\dots \text{g/L.}$$

Date:

Experiment:

Date:

Experiment:

