Module 5- Phase Rule and Analytical Techniques

SYLLABUS:

Phase rule: Introduction, Definition of terms: phase, components, degree of freedom, Phase rule equation. Phase diagram: Two component-lead-silver system.

Analytical techniques: Introduction, principle, instrumentation of potentiometric sensors and its application in the estimation of iron, conductometric sensors and its application in the estimation of acid mixture, pH sensors and its application in the determination of soil sample.

Self-learning: Chromatographic technique, application of chromatography (column and thin layered chromatography) in the separation of components

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Phase Rule

Phase rule is mathematical equation that relates number of degree of freedom, phase and components.

It is defined as **"for a heterogeneous system in equilibrium, the number phases plus the number of degree of freedom is equal to the number of components plus two"**

i.e $P + F = C + 2$

terms involved:

Phase: it is a homogeneous part of heterogeneous system which can be physically separable and remains physically distinct.

Example1: mixture of gas, here only one phase is seen.

Example 2: In a saturated solution of salt two phases are seen. Liquid and solid

Example 3: A equilibrium that exists between ice, water and vapor, here three phases are seen . solid, liquid and gas.

Example 4: mixture of oil and water or benzene and water, here we can see two phases.

Component: it is the minimum number of independent constituents present which are necessary and sufficient to express the composition of all the phase present in the system.

Example: consider the equilibrium between ice ↔ water ↔ vapor, this is one component system as all the phases made up of water.

Degree of freedom: the minimum number of variables like temperature, pressure and composition of the components which must be specified to define the system completely is called degree of freedom.

If F= 1 it is called univariant system.
F= 2 bivariant system.
F= 0 it is invariant system.

Lead- silver system (two component system)

In two component system when the number of phases is one and degree of freedom is three. All the three variables are necessary to define any single phase in a two-component system which is bit difficulty so in order to simplify this pressure is kept constant.

For two component system under constant pressure the phase rule is modified as
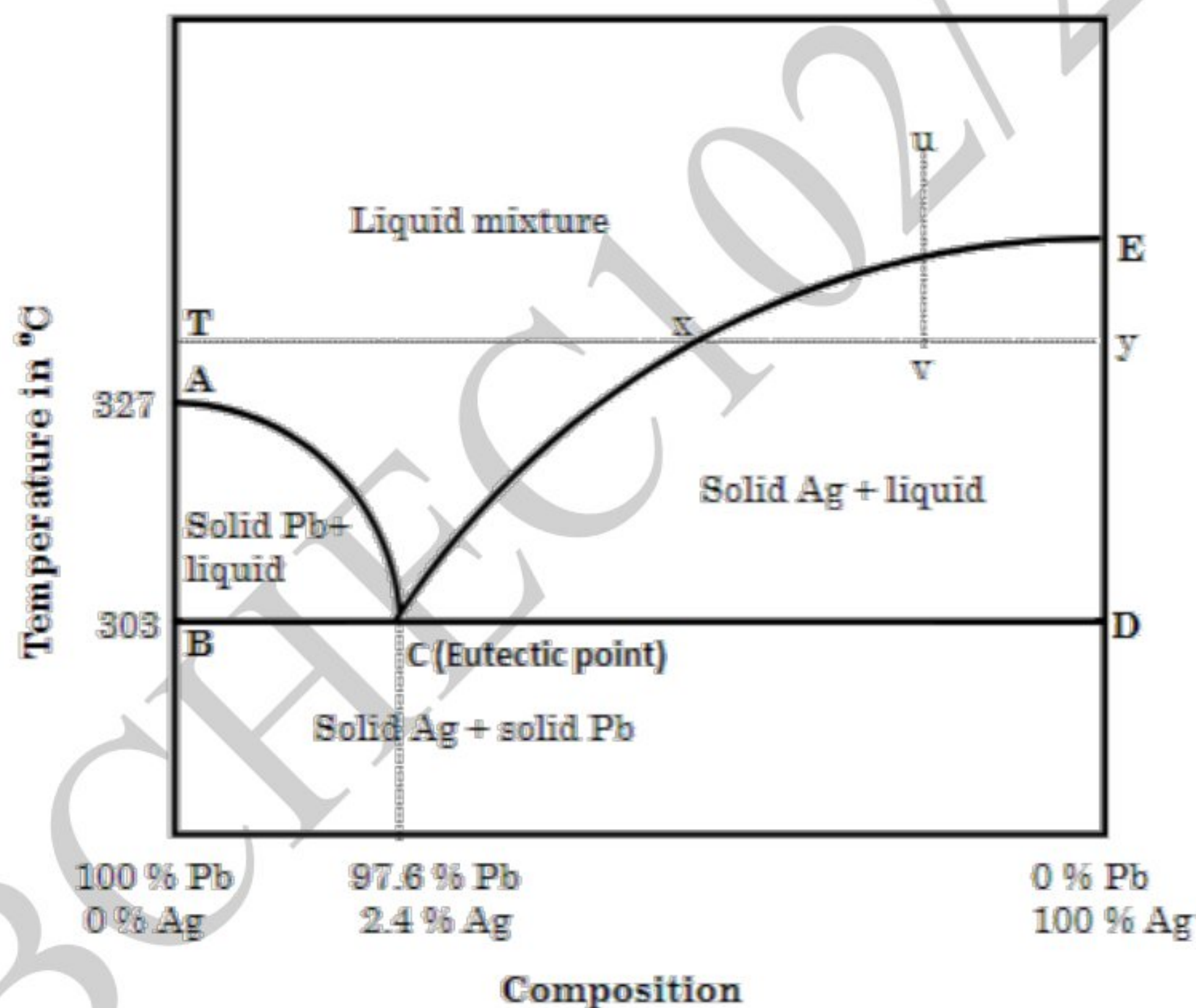
P+ F' = C+ 1

P + F' = 2+ 1

P + F' = 3

The above equation is called **"condensed phase rule."**

Lead- silver is a two-component system here the two components are completely miscible in the liquid state and pure components crystallize from the solution on careful cooling.

Phase diagram for Pb-Ag system

The phase diagram is obtained by plotting the temperature against the percentage composition of mixture of Pb and Ag.

It consists of:
1) Areas: ACE, ACB and ECD
2) Lines: AC and EC
3) Eutectic point: C

Areas: consider the area ACE, it represents the liquid phase consisting of completely miscible molten Pb and molten Ag.

Here P= 1, C= 2

From the condensed phase rule, P +F' = C+1

$$= 1 + F' = 2 +1$$
$$= F' = 2$$

There for the system is bivariant and both temperature and % composition is needed to define the system.

Consider the **area ACB and ECD**, it represents solid lead and liquid and solid silver and liquid respectively.

From the condensed phase rule, P +F' = C + 1

$$= 2 +F' = 2 +1$$
$$= F' = 1$$

There for the system is univariant. Either temperature or %composition is enough to define the system.

Suppose the liquid mixture is gradually cooled no solid separates out till the point v. at point v the solid Ag separates out.

Lines: AC is the freezing point curve of lead. And line EC is freezing pint curve of silver.

Here P = 2, C = 2

From the condensed phase rule

P + F' = C + 1

2 + F' = 2 + 1

F' = 1

There for the system is univariant and hence either temperature or %composition is enough to define the system.

Eutectic point (C): point c is the eutectic point where equilibrium exists between sold Ag , solid Pb and liquid mixture. Here the composition of Ag will be 2.4% and composition of Pb will be 97.6%.

here P = 3, C = 2

from the condensed phase rule

P + F' = C + 1

3 + F' = 2 + 1

F' = 0

There for the system is invariant. And no need to specify the temperature or %composition here as it is fixed.

If the temperature at the eutectic point is lowered, the liquid will disappear and the entire mass separates as a mixture of solid Pb and Ag.

Applications of Phase diagram:

- Useful for selection of alloys with a specific composition to produce specific properties.
- To predict the phase changes that have occurred in an alloy that has been exposed to a particular eat treatment.

Analytical Techniques:

Analytical chemistry methods refer to techniques used for the detection, identification, characterization, and quantification of chemical compounds. Qualitative identifies analytes, while quantitative analysis determines the numerical amount or concentration. Several Instruments and sensors are being used for analysis as these methods are faster, accurate and require a minimum quantity for analysis. Instrumental methods such as conductometry and potentiometry are some examples of these methods.

Conductometry

Principle/ Theory

Conductometric titrations are the titrations in which the amount of the analyte present in the given solution is measured by the change in conductance. The principle underlying conductometry is the measurement of replacement of ions of a particular conductivity by ions of different conductivity during a chemical reaction. Conductivity electrodes or sensors are used to determine the end point in acid base titrations. Neutralization point is determined by observing the change in specific conductance of the solution. Specific conductance(K) is the conductance of a solution present between 2 parallel electrodes of area 1cm² which are kept 1cm apart. Here R is the resistance.

$$K = \frac{1}{R} X \frac{1}{a} \qquad \left[\frac{1}{a} = \text{cell constant} \right]$$

The specific conductance of an electrolytic solution at any temperature depends on ions present and hence varies with ionic concentration. The measurement of conductance is used to determine the equivalence point in acid base titrations. In conductometric titration, there is a sudden change in conductance of solution at equivalence point. Hence equivalence point is determined by plotting a graph of conductance versus volume. Therefore, the concentration of the analyte in the solution can be calculated.

Instrumentation

The conductor consists of 2 platinum electrodes and a conductance measuring device. The 2 electrodes have unit area of cross section and are placed unit distance apart. The solution to be estimated is taken in a beaker. The system responds readily to changes in concentration of analyte.

To, conductometer

Stirrer

1cm² 1cm

Platinum electrode
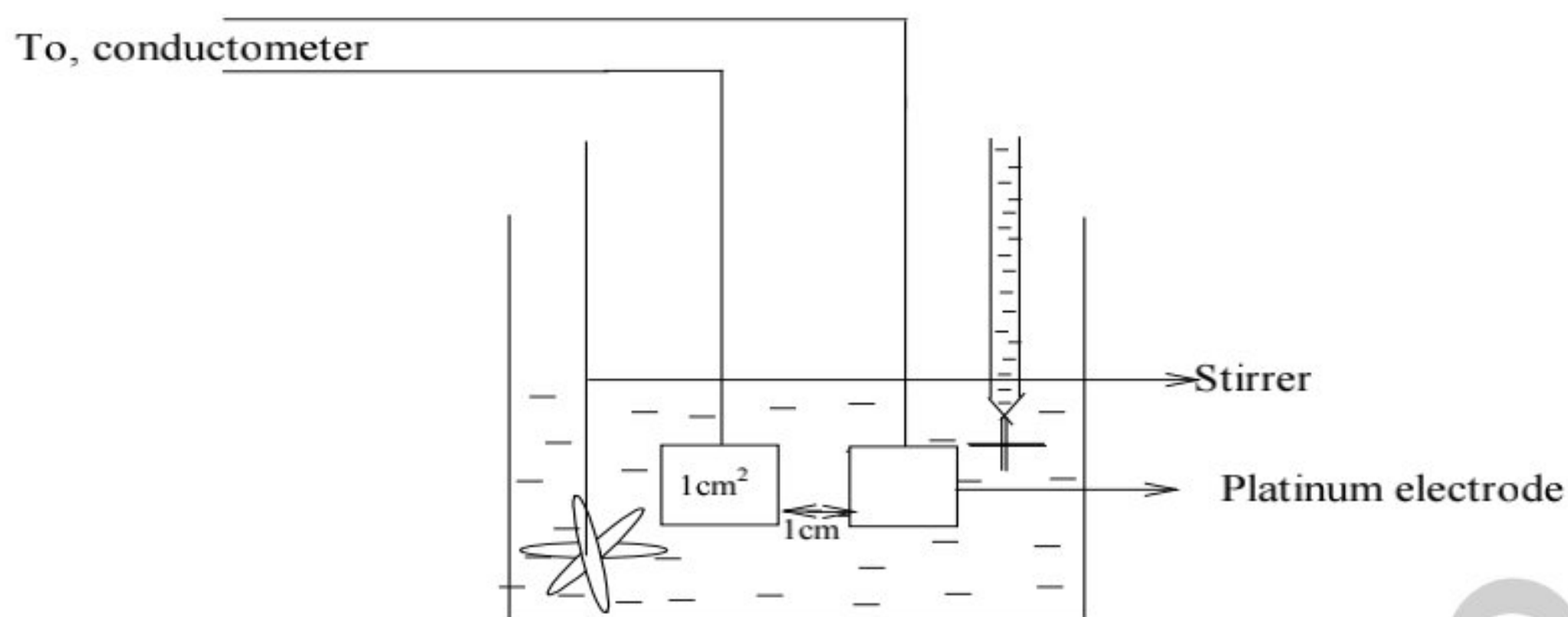
Advantages

✓ Mixture of acids can be titrated accurately.

✓ Accurate results are obtained in dilute as well as more concentrated solutions.

✓ The method can be employed for colored solutions also.

Application: estimation of acid mixture

Titration of acid mixture with strong base:

- In the mixture of strong acid and weak acid, strong acid dissociates completely and is consumed first by the base.
- After the neutralization of strong acid, the weak acid is neutralized.
- During neutralization of the strong acid (Ex: HCl) conductance first falls since highly mobile H^+ ions are replaced by Na+ of base.
- Later, during the neutralization of weak acid (Ex: acetic acid), the poorly conducting acid is converted. Into salt (Ex. CH_3COONa). The salt undergoes complete dissociation; therefore, **the** conductance increases gradually.
- After the complete neutralization, further addition of base NaOH introduces more and more Na+ and OH- ions into the solution, conductance again increases rapidly.
- When conductance of the solution is plotted against volume of base added, three straight lines will be obtained. The first point of intersection corresponds to the volume of base required to neutralize strong acid and second point of intersection is for total acid.

equivalence point for strong acid
equivalence point for total acid

Vol. of base ⟶

Conductance ⟶
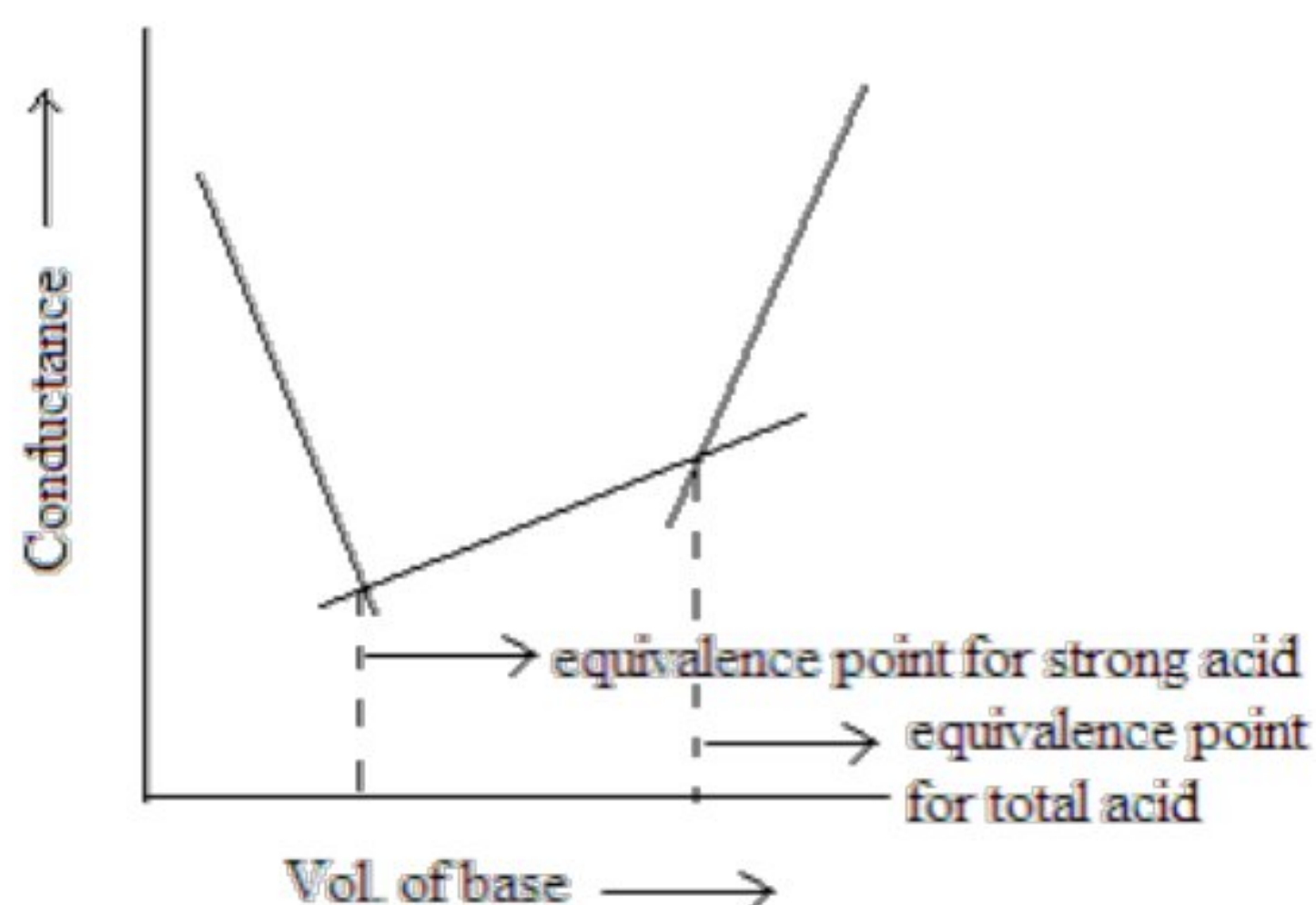
Potentiometry

Principle

In potentiometric titrations, concentrations of the solutions can be calculated by measuring the emf between two electrodes dipped in the analyte solution.

The potential of an electrode is given by Nernst equation,

$$E = E^o + \frac{0.0591}{n} \log \left[M^{n+} \right]$$

i.e., The potential of an electrode depends on the concentration of ion to which it is reversible. This method can be used in the determination of end points of acid-base titrations, red-ox titrations etc. When a known volume of analyte is titrated with a standard solution, neutralization or red-ox reaction takes place. During titration, concentration of product will be continuously altered. If a metal electrode, reversible with respect to corresponding ions is placed in the solution, the potential will vary throughout the titration, which can be determined using a suitable device. Initially, the change in potential is very small. At the equivalence point, when the amount of titrant added is equivalent to the amount of analyte present, there will be a sharp rise in potential. Beyond the equivalence point, there will be no significant change in potential. By plotting a graph of change in potential against the volume of titrant added, the equivalence point can be determined.

Instrumentation

Potentiometer consists of a reference electrode, an indicator electrode, and a potential measuring device. The indicator electrode (platinum electrode) responds to the changes in concentration of analyte. A reference electrode like saturated calomel electrode is also used. A known volume of analyte is taken in the beaker and its potential is determined. The titrant is added in increments of 0.5 ml and emf is measured each time. At equivalence point, emf increases rapidly. At this point, titrant is added in small increments of 0.5ml. a few readings are taken beyond the end point. Thus, the changes in potential at different volumes of titrant are recorded.

To, potentiometer

Indicator electrode

Reference electrode

Stirrer
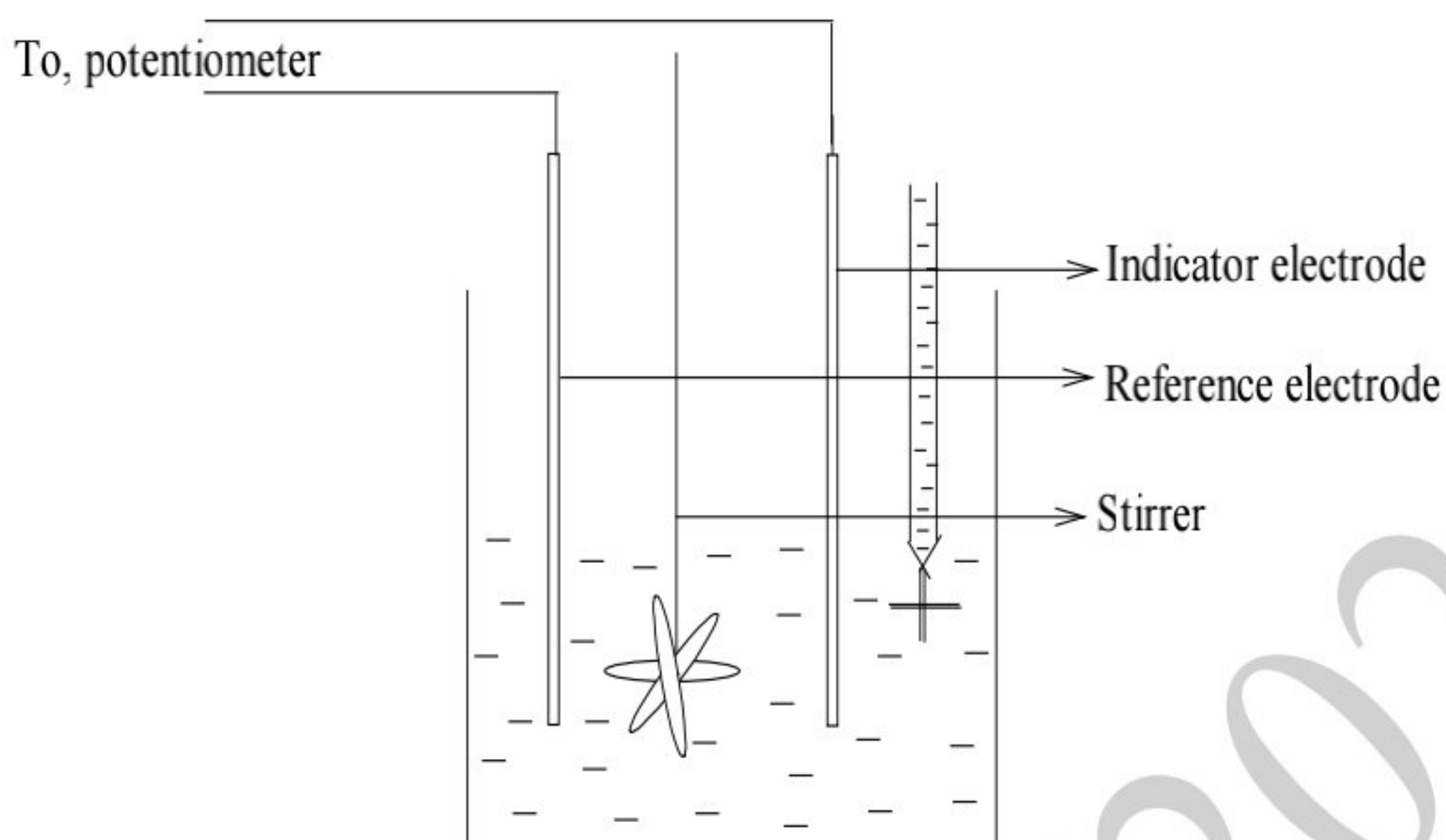
Advantages:

✓ Potentiometric titrations can be carried out in colored solutions where indicators cannot be used.

✓ By potentiometry, it is possible to determine the end point in titrations of redox, precipitation and acid-base titrations.

Application:

Estimation of Iron (Fe) using acidified Potassium dichromate solution

Potentiometry can be used to determine the end point of a redox titration by measuring the change in potential during titration using a platinum-calomel electrode combination.

The titrations involving Mohr's salt solution and Potassium dichromate solution can be done by Potentiometry.

- The platinum electrode is used as an indicator electrode and coupled with a calomel electrode (reference electrode) and dipped in a solution of known volume of analyte (Mohr's salt solution) and connected to potentiometer and emf is measured.

- The titrant (Potassium dichromate) of known concentration is added in increments of 0.5ml from burette to the analyte solution and emf is measured each time after stirring the solution.

- FAS reacts with $K_2Cr_2O_7$ under acidic conditions, the redox electrode potential is set up at indicator electrode. $Pt/Fe^{2+}, Fe^{3+}$.

- The electrode potential of the redox electrode is given by Nernst equation.

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[\ Fe^{3+}\ ]}{[\ Fe^{2+}\ ]}$$

- The electrode potential depends upon concentration of Fe^{2+} and Fe^{3+},

- As the titration proceeds Fe^{3+} increases and Fe^{2+} decreases and redox electrode potential increases and emf of the cell goes on increasing and steep rise is seen at equivalence point.

- At equivalence point all the Fe^{2+} is converted to Fe^{3+} ions and redox potential of Pt/Fe^{2+}, Fe^{3+} stops and further addition of dichromate new redox potential comes into existence Pt/Cr^{6+}, Cr^{3+} because the solution contains Cr^{3+} ions produced due to reduction of dichromate by Fe^{2+} ions. This redox electrode Pt/Cr^{6+}, Cr^{3+} has higher potential than Pt/Fe^{2+}, Fe^{3+}.

- Plot a graph of $\Delta E/ \Delta V$ versus volume of $K_2Cr_2O_7$ gives the equivalent point.
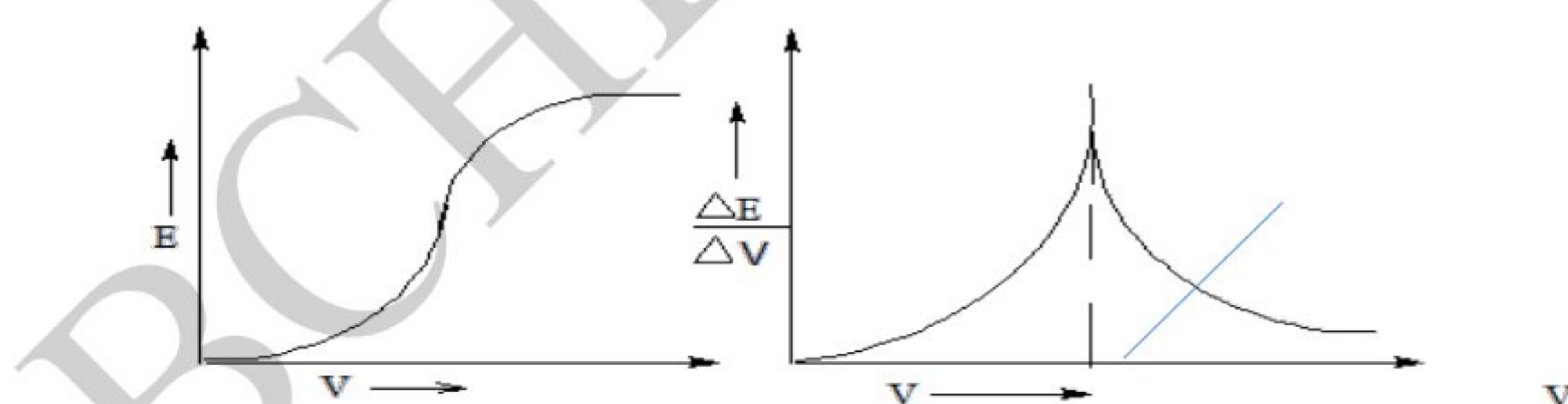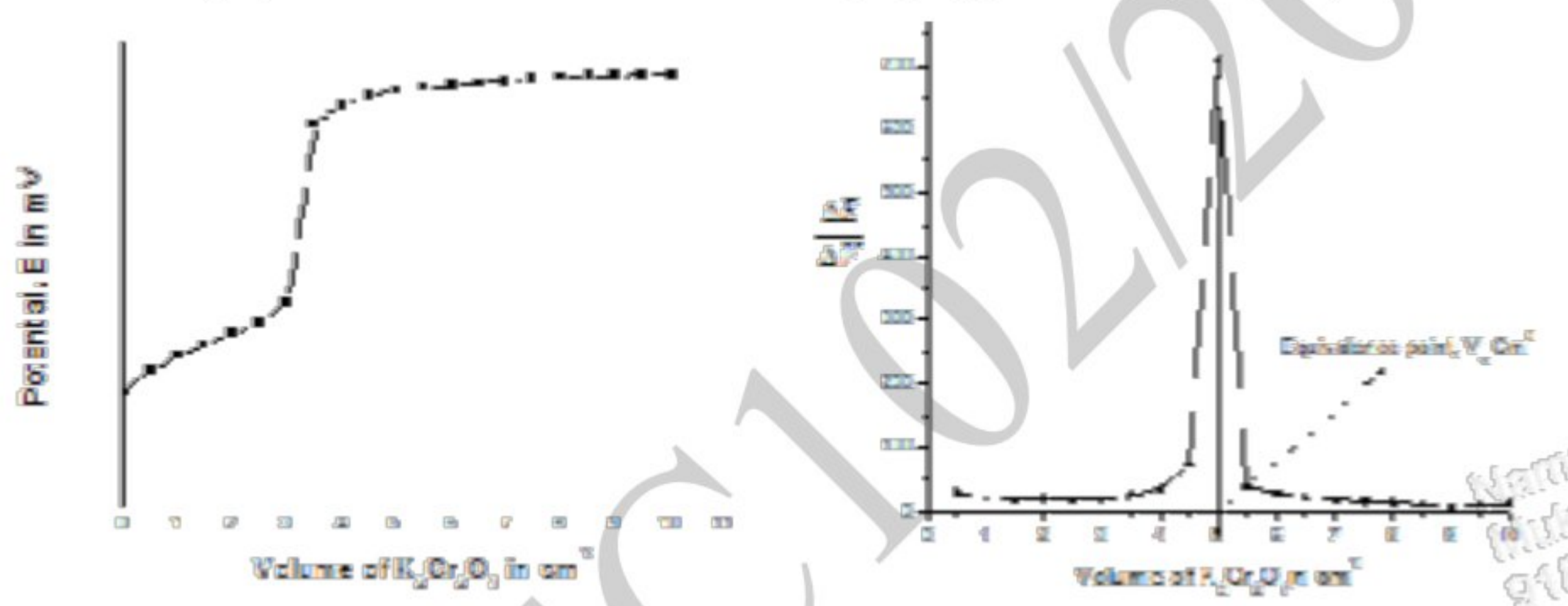
pH sensor and its application in the determination of pH of soil.

➢ The most accurate method of determining soil pH is by using the pH meter and pH sensor.

➢ Glass pH electrode is the pH sensor used.

➢ Glass electrode is an ion selective electrode which is more selective towards H^+ ions.

➢ In order to measure the pH of a beverage or any other unknown solution a galvanic cell is constructed by using saturated calomel electrode (reference electrode) and a glass electrode.

➢ Galvanic cell is represented as

Hg/ HgCl₂/ KCl / solution of unknown pH / glass membrane/ HCl / AgCl /Ag

Schematic representation
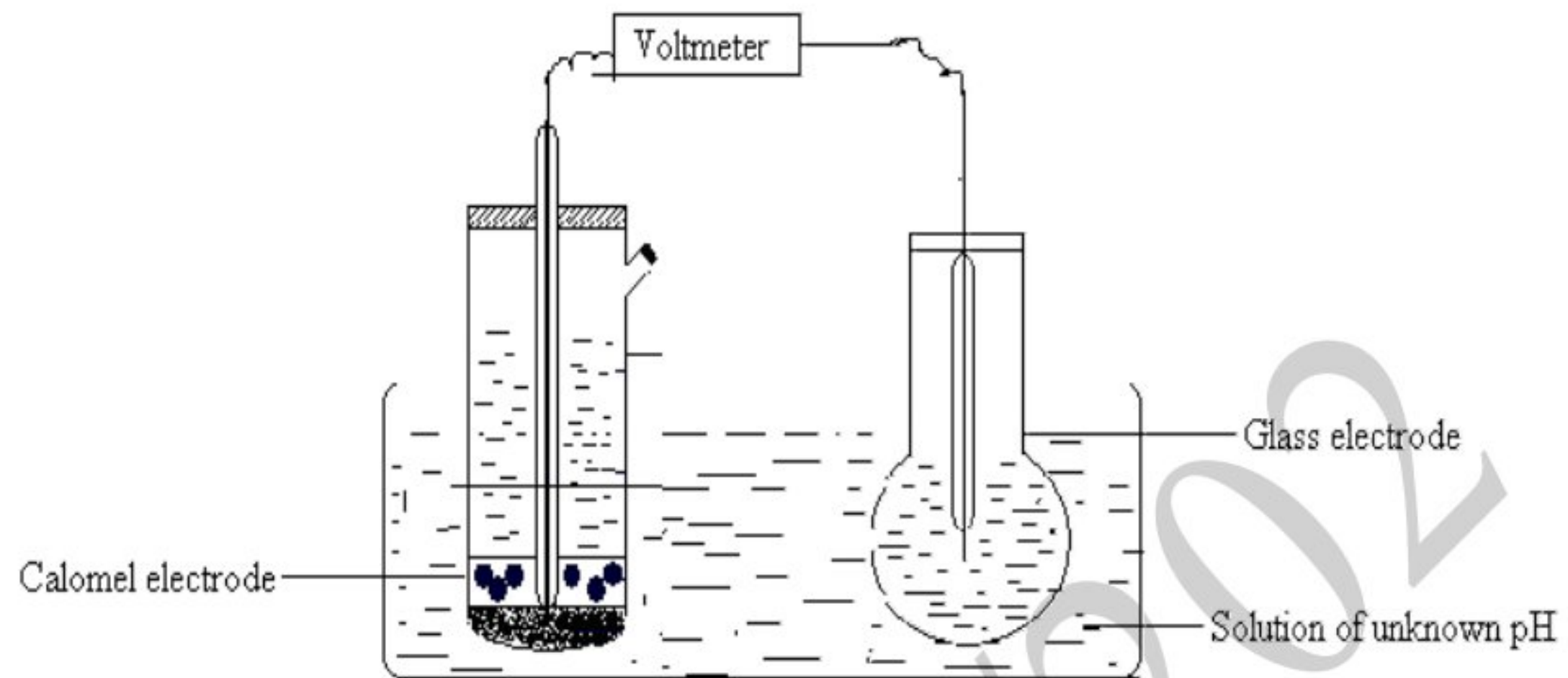
- ➤ <u>EMF</u> of the cell is measured using a highly sensitive voltmeter.
- ➤ EMF of the cell is measured using two times. First by immersing the cell in an unknown solution and secondly in known pH of buffer.
- ➤ EMF of the cell can be calculated using the formula (for unknown solution)

$$E_{cell\ (u)} = E_{cathode} - E_{anode}$$

$$= E_{glass} - E_{SCE}$$

$$= L' - 0.0591\ pH(u) - E_{SCE}$$

$$E_{cell\ (u)} = K - 0.0591 pH_{(u)} \ \text{------>}\ eq1$$
$$\text{(where K is a constant and K= L'-E}_{SCE}\text{)}$$

The value of K can be determined by measuring EMF of the galvanic cell immersed in standard buffer solution of known pH.

$$K = E_{cell\ (b)} + 0.0591\ pH_{(b)}$$

On substituting the value of K in equation 1

$$E_{cell(u)} = E_{cell(b)} + 0.0591 pH_{(b)} - 0.0591\ pH(u)$$

$$0.0591\ pH_{(u)} = E_{cell(b)} + 0.0591 pH_{(b)} - E_{cell\ (u)}$$

$$pH_{(u)} = pH_{(b)} + \frac{E_{cell\ (b)} - E_{cell\ (u)}}{0.0591}$$

Thus pH of soil sample solution can be determined by measuring EMF of the above galvanic cell immersed in buffer solution and then in solution of unknown pH..

Question Bank

1. Define phase rule. Explain the terms involved in it with examples.

2. Explain the phase rule for Lead-Silver system (two component)

3. Explain the principle, instrumentation, and application in estimation of acid mixture using conductometric sensors.

4. Explain the principle, instrumentation, and application in estimation of amount of iron (Fe) /ferrous using potentiometric sensors.

5. What is a pH sensor? Explain the determination of pH of soil sample using pH sensors.