SEMESTER-I

Physical properties:
♦ Determination of density, surface tension and viscosity of liquids

Distribution:
♦ Distribution of acetic acid between n-butanol and water
♦ Distribution of iodine between CCl₄ and water

Chemical kinetics:
♦ Acid-catalyzed hydrolysis of methyl acetate
♦ Peroxydisulphate- I⁻ reaction (overall order)
♦ Oxidation of iodide ion by hydrogen peroxide- iodine clock reaction

Conductometry:
♦ Titration of strong acid vs. strong base
♦ Titration of weak acid vs. strong base
♦ Determination of cell constant
♦ Determination of dissociation constant of a weak acid

Potentiometry:
♦ Titration of strong acid Vs strong base
♦ Titration of weak acid Vs strong base
♦ Determination of dissociation constant of a weak acid
♦ Determination of single electrode potential

Polarimetry:
♦ Determination of specific rotation of sucrose
♦ Acid-catalyzed hydrolysis of sucrose (inversion of sucrose)

Adsorption and others:
♦ Adsorption of acetic acid on animal charcoal or silica gel
♦ Determination of critical solution temperature of phenol-water system
♦ Effect of added electrolyte on the CST of phenol-water system.
SEMESTER-II

Distribution:
1. Distribution of I₂ between CCl₄ and aq.KI solution- calculation of equilibrium constant.

Chemical Kinetics
1. Stoichiometry of peroxydisulphide- iodide reaction
2. Peroxydisulphide- iodide reaction: order w.r.t [I⁻] by isolation method
3. Peroxydisulphide- iodide reaction: order w.r.t [S₂O₈²⁻] by initial rate method

Conductometry:
1. Titration of a mixture of strong and weak acids vs strong base
2. Determination of the hydrolysis constant of aniline hydrochloride
3. Determination of solubility product

Potentiometry:
1. Titration of Fe²⁺ vs Cr₂O₇²⁻ (redox titration)
2. Titration of Cl⁻ vs Ag⁺ (precipitation titration)
3. Determination of solubility product

Polarimetry:
1. Determination of specific rotation of glucose and fructose
2. Enzyme catalysed inversion of sucrose

Colorimetry:
1. Verification of Beer’s law and calculation of molar absorption coefficient using CuSO₄ and KMnO₄ solutions

pH metry:
1. Preparation of phosphate buffers
Semester-I

1. DETERMINATION OF PHYSICAL CONSTANTS/SURFACE TENSION

**Aim:** To determine the surface tension of the given liquids using pyknometer.

**Apparatus:** Pyknometer, clamp, rubber tubes weight box.

**Chemicals:** Benzene, carbon tetra chloride, n-hexane,

**Principle:** All the molecules in a liquid are held together by force of attraction and this causes the surface of the liquid to behave like a stretched skin. Surface tension is the result of the force of attraction b/n the molecules present on the surface.

It is the force of acting per unit length of the surface of the surface of the liquid.

The formation of drops depends on the surface tension of the liquid and all liquids will not give same number of drops from same volume of liquid.

The surface tension of a given liquid can be evaluated by using the equation

\[ n_2 = n_1 x d_2 \]

\[ n_1 = \frac{n_2 x d_1}{d_2} \]

Where \( n_2 = \) is the surface tension of the given liquid.

\( n_1 = \) is the surface tension of water.

\( n_1 = \) is the no. of drops for water.

\( n_2 = \) is the no. drops for the given liquid.

\( d_1 = \) is the density of water.

\( d_2 = \) is the density of the given liquid.
**Procedure: Description of stalagmometer:**

It consists of a fine capillary tube with a bulb at the centre. The upper end of the tube is fitted with a rubber tube which is used to suck the liquid. The lower end of the tube consists of a fine capillary bore. The upper and lower ends of the bulb contain two marks say A and B.

Clean the stalagmometer thoroughly with distilled water followed by chromic acid and again with distilled water. Now suck the distilled water through the upper end slight above the mark A and tighten the rubber tube with a pinch cock. Clamp the stalagmometer and release the pinch cock. Count the number of drops till the liquid reaches the lower mark B repeat the procedure and measure the no. of drops and the mean of the readings is taken into account.

Now discard water and dry the tube by using dry air current or in the oven. Repeat the procedure with the other given liquids and tabulate the results. Knowing the density values of the respective liquids calculate the surface tension using the above given formula.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>liquid</th>
<th>No. of drops ($n_1$)</th>
<th>No. of drops ($n_2$)</th>
<th>Mean ($\frac{n_1 + n_2}{2}$)</th>
<th>Surface Tension (n)</th>
<th>Literature Value</th>
<th>% error</th>
</tr>
</thead>
</table>

**Result:** Surface tension of the given liquids.
DISTRIBUTION:

2. DISTRIBUTION OF ACETIC ACID BETWEEN n-BUTANOL AND WATER

Aim: To determine distribution coefficient of Acetic acid between n-Butanol and water by verifying Nernst distribution law

Apparatus: Reagent bottle, Burette, Pipettes, Conical flasks & measuring jar

Chemicals: 2M Acetic acid, n-Butanol, 0.25M NaOH & Phenolphthalein indicator

Principle: When a common solute is added to a system of two immiscible liquids, solute distributes itself in a definite concentration ratio such way that its concentration ratio is constant at constant temperature irrespective of the amount of solute is added.

The Distribution coefficient is given by

\[ K_D = \frac{C_{aq}}{C_{org}} \]

\[ \log C_{aq} = \log K_D + \log C_{org} \]

Where \( C_{org} \) & \( C_{aq} \) are concentrations of solute in organic & aqueous layers respectively

Procedure: Take 40mL of n-Butanol, 40mL of distilled water in a clean reagent bottle and add 2M AcOH to the same reagent bottle. Shake vigorously about 15 minutes for proper distribution. Allow the reagent bottle for the layers to separate. Meanwhile fill the burette with 0.25M NaOH. Now pipette out 10mL of Organic (upper) & Aqueous (lower) layers into two conical flasks separately. Titrate both the layers against 0.25M NaOH Solution by adding 2-3 drops of Phenolphthalein indicator. Note down the readings as \( V_{org} \) & \( V_{aq} \) respectively.

Now add 10mL of n-Butanol & 10mL of distilled water to the reagent bottle. Shake vigorously about 10 minutes for proper distribution. Do the titrations as...
mentioned earlier. Repeat the same experimental procedure for both the layers (4-6 times) and then calculate concentrations of Acetic acid.

**Note:** Density of Water = 1.028 gm/ml; Density of n-Butanol = 0.811 gm/ml

**Model graphs:** Plot a graph between $C_{aq}$ and $C_{org}$, straight line passing through origin is obtained. From the slope distribution constant ($K_D$) can be calculated.

![Graph](image_url)

**Model tabular form:**

<table>
<thead>
<tr>
<th>S.No</th>
<th>$V_{org}$</th>
<th>$V_{aq}$</th>
<th>$C_{org}$</th>
<th>$C_{aq}$</th>
<th>log $C_{aq}$</th>
<th>log $C_{org}$</th>
<th>$K_D = C_{aq}/C_{org}$</th>
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</table>
**Result:** Nernst Distribution law is verified.

- \( K_D \) (From calculations) = ..............
- \( K_D \) value from Graph -1 = ....................
- \( K_D \) value from Graph -2 = ....................
- Slope value from graph-2 = ....................

Therefore, Acetic acid exists as a monomer in the organic layer.
3. DISTRIBUTION OF I$_2$ BETWEEN CCl$_4$ AND WATER

**Aim:** To determine distribution coefficient of I$_2$ between CCl$_4$ and water by verifying Nernst distribution law

**Apparatus:** Reagent bottle, Burette, Pipettes, Conical flasks & measuring jar

**Chemicals:** Saturated I$_2$/CCl$_4$, M/20 Hypo, M/600 Hypo Starch indicator

**Principle:** When a common solute is added to a system of two immiscible liquids, solute distributes itself in a definite concentration ratio such way that its concentration ratio is constant at constant temperature irrespective of the amount of solute is added.

The Distribution coefficient is given by

$$K_D = \frac{C_{aq}}{C_{org}}$$

$$\log C_{aq} = \log K_D + \log C_{org}$$

Where $C_{org}$ & $C_{aq}$ are concentrations of solute in organic & aqueous layers respectively
**Procedure:** Take 25mL of I₂/CCl₄ and add 25mL of distilled water in a clean reagent bottle. Shake vigorously about 15 minutes for proper distribution. Allow the reagent bottle for the layers to separate. Meanwhile fill the burettes with M/20 Hypo M/600 Hypo. Now pipette out 10mL of organic (lower) & 10mL of aqueous (upper) layers into two conical flasks separately. Titrate organic layer with M/20 Hypo solution and titrate aqueous layer with M/600 Hypo solution by adding 2-3 drops of Starch indicator. Note down the readings as $V_{org}$ & $V_{aq}$ respectively.

Now add 10mL of CCl₄ & 10mL of distilled water to the reagent bottle. Shake vigorously about 10-15 minutes for proper distribution of solute between two layers. Do the titrations as described above. Repeat the same experimental procedure for both the layers (4-6 times) and then calculate concentrations of Iodine as $C_{org}$ & $C_{aq}$ respectively.

**Note:** Density of Water = 1.028 gm/ml; Density of CCl₄ = 1.59 gm/ml

**Model graphs:** Plot a graph between $C_{aq}$ and $C_{org}$, straight line passing through origin is obtained. From the slope distribution constant ($K_D$) can be calculated.
Model tabular form:

<table>
<thead>
<tr>
<th>S.No</th>
<th>$V_{org}$</th>
<th>$V_{aq}$</th>
<th>$C_{org}$</th>
<th>$C_{aq}$</th>
<th>$\log C_{aq}$</th>
<th>$\log C_{org}$</th>
<th>$K_D = \frac{C_{aq}}{C_{org}}$</th>
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</table>

**Result:** Nernst Distribution law is verified.
\[ K_D \text{ (From calculations)} = \quad \ldots \ldots \ldots \]

\[ K_D \text{ value from Graph} \ -1 = \quad \ldots \ldots \ldots \ldots \]

\[ K_D \text{ value from Graph} \ -2 = \quad \ldots \ldots \ldots \ldots \]

**Chemical Kinetics:**

**1. Acid-catalyzed hydrolysis of Methyl acetate:**

**Aim:** To Study the Acid catalyzed hydrolysis of an ester (Methyl Acetate) under Pseudo conditions (first order reaction) and determine the rate constant \( k \)

**Apparatus:** Burette, Pipette, Conical flask, Reagent bottles etc

**Chemicals:** Methyl Acetate, HCl (1M/2M), NaOH (0.5M), Phenolphthalein indicator, crushed ice.

**Principle:** Hydrolysis of an ester in aqueous medium is very slow. Hence the reaction rate is enhanced by an acid (HCl). The reaction is as follows
\[
\text{Methyl acetate} + \text{H}_2\text{O} \xrightleftharpoons{H^+} \text{Acetic acid} + \text{MeOH}
\]

Rate = \(k^1 \left[\text{Ester}\right] \left[H_2\text{O}\right]\)

Rate = \(k \left[\text{Ester}\right]^1 \) \(\text{(where } k = k^1 \left[H_2\text{O}\right]\text{)}\)

\(k = \text{Pseudo first order rate constant}\)

The reaction is of 1\(^{st}\) order with respect to Methyl Acetate, since the concentration of water is taken in large excess and hence the change in water concentration is very less or virtually constant during the course of the reaction. Hence the reaction is referred as Pseudo first order reaction.

Rate constant,

\[
k = \frac{2.303}{t} \log \left[\frac{V_0 - V_o}{V_0 - V_t}\right] \text{ min}^{-1}
\]

\textbf{Procedure:} Take 100 ml of 1M HCl in a clean reagent bottle and fill the burette with 0.5MNaOH solution. Now add 10 ml of pure Methyl Acetate to the reagent bottle containing HCl and shake the solution. Immediately (within 10-15 seconds), pipette out 10 ml of the reaction mixture into a clean conical flask containing ice cold water in order to quench the reaction. Now add 2 or 3 drops of Phenolphthalein indicator and titrate against NaOH solution. Note down the titre value in the tabular form as \(V_o\). Repeat the same titration procedure for every 10 minutes of regular intervals of time by doing up to 60 minutes. Tabulate the titre values as \(V_t\).

\textbf{For } V_\infty: \text{ Heat the remaining reaction mixture for half an hour by maintaining 50 – 60°C. Cool it to room temperature under tap water. Pipette out 10 ml of the above reaction mixture into a clean conical flask (without ice water) and titrate against NaOH solution using phenolphthalein indicator. Take the titre value as } V_\infty.
Repeat the same experimental procedure for 2M HCl solution and tabulate the data

**Model Graphs:** Plot a graph between \( \log \left( \frac{V_\infty - V}{V_\infty - V_t} \right) \) and time, straight line passing through origin is obtained. From the slope rate constant \( k \) can be calculated. Plot another graph between \( \log (V_\infty - V_t) \) and time, a straight line with negative slope is obtained.

**Model tabular form:**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (min)</th>
<th>Volume of NaOH (ml)</th>
<th>((V_\infty - V_t))</th>
<th>(\log(V_\infty - V_t))</th>
<th>(\frac{V_\infty - V}{V_\infty - V_t})</th>
<th>(\log \left( \frac{V_\infty - V}{V_\infty - V_t} \right))</th>
<th>(k = \frac{2.303}{\text{Time (min)}} \log \left( \frac{V_\infty - V}{V_\infty - V_t} \right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
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</table>
Result:

The reaction is of Pseudo first order.

Rate constant from the experiment data = ………………………….. min$^{-1}$

Rate constant from the graph - 1 = ………………………….. min$^{-1}$

Rate constant from the graph - 2 = ………………………….. min$^{-1}$
2. Peroxydisulphate- Iodide reaction

Determination of overall order rate constant of a reaction

**Aim:** To verify the order and determine the rate constant by following the kinetics of potassium Persulphate and Potassium iodide reaction volumetrically.

**Apparatus:** Iodination flask, burette, pipette, standard flask, conical flask, beaker, beaker, measuring jar, stop watch etc.

**Chemicals required:** 0.1M KI, 0.05M K$_2$S$_2$O$_8$, M/200 hypo, Ice cold water, starch indicator.

**Principle:**

**Chemical reaction:**   
$\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$

$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$

**Mechanism:** 
$\text{S}_2\text{O}_8^{2-} + \text{I}^- \rightarrow (\text{S}_2\text{O}_8\text{I})^{-3}$

$(\text{S}_2\text{O}_8\text{I})^{-3} + \text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$

Adding the above two equations,

$2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$

This is a reaction of the second order as the concentrations of both the reactants appear in the rate equation to first power. During the reaction, iodine is liberated and progress of the reaction is observed by titrating the liberated iodine against sodium thiosulphate solution (hypo) at regular intervals of time. The titre values are proportional to iodine formed and therefore to the amount of peroxy disulphate which has disappeared.

A known quantity of K$_2$S$_2$O$_8$ is mixed with definite known quantity of KI. Let the initial concentration of K$_2$S$_2$O$_8$ be ‘a’ moles per litre; ‘x’ be the concentration of I$_2$ formed in the reaction at any time,‘t’. $V_t$ is the volume of hypo required at any time ‘t’ and $V_\infty$ is the volume of hypo required at the end of the reaction. Then the reaction follows second order and the rate law is given by:
Rate = $k_2 [\text{KI}] [\text{K}_2\text{S}_2\text{O}_8]$ 

$$\frac{x}{x(a-x)} = \left[ \frac{1}{(a-x)} - \frac{1}{a} \right] = k_2 t$$

Which may be expressed in terms of volumes $V_t$ and $V_\infty$ as:

$$\frac{V_t}{V_\infty (V_\infty - V_t)} = k_2 t$$

$$k_2 = \frac{1}{t} \left[ \frac{V_t}{V_\infty (V_\infty - V_t)} \right]$$

**Procedure:** Take 50ml of 0.05M K$_2$S$_2$O$_8$ into an iodination flask. Fill the burette with M/200 hypo. Keep a conical flask ready for titration, with some ice cold water and a few ice pieces in it. Now measure 50ml of 0.1M KI, add it to the iodination flask containing K$_2$S$_2$O$_8$ and immediately note down the time. After 10 minutes pipette out 10ml of reaction mixture into a conical flask containing ice cold water and add few drops of freshly prepared starch solution. The solution turns blue. The end point is indicated by the disappearance of blue colour. Note down the titre value, $V_t$ for 10 minutes. And repeat the similar procedure and determine $V_t$ corresponding to the times 20, 30, 40 .... minutes respectively.

**For $V_\infty$ value:** At the early stage of the reaction i.e., after 2 to 3 minutes, pipette out 10ml of the reaction mixture into a clean conical flask and add excess of KI to it (one spatula of solid KI) cover it with watch glass and keep it in dark for about 30 minutes. After 30 minutes take out the flask and wash the lid of watch glass into the conical flask. Titrate the contents of the conical flask against hypo and note down the reading as $V_\infty$. 
**Model tabular form:**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Volume of hypo required (mL)</th>
<th>$\frac{1}{V_\infty - V_t}$</th>
<th>$\frac{V_t}{V_\infty (V_\infty - V_t)}$</th>
<th>$k_2 = \frac{1}{t} \left[ \frac{V_t}{V_\infty (V_\infty - V_t)} \right]$</th>
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<td>$V_\infty =$</td>
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</table>

**Model graph:** Plot a graph between $\frac{V_t}{V_\infty (V_\infty - V_t)}$ Vs time, a straight line passing through origin is obtained, slope of the line is equal to $k_2$. Draw another plot between $\frac{1}{V_\infty - V_t}$ Vs time, a straight line with positive slope and intercept is obtained.

**Graph:1**

![Graph 1](image1)

**Graph:2**

![Graph 2](image2)
Result:  
k₂ value from calculations = ................ lit/mole/min

From Graph – 1, k₂ =

From Graph – 2, k₂ =
3. Oxidation of Iodide ion by H$_2$O$_2$- Iodide clock reaction:

**Aim:** Study of oxidation of iodide ions by hydrogen peroxide as an iodine clock reaction.

**Apparatus:** Burette, 5ml pipette, 250ml measuring jar, 500ml conical flask, stop watch.

**Chemicals:** 0.1M H$_2$O$_2$, 1.0M KI, 2M H$_2$SO$_4$, 0.025M hypo, starch solution.

**Principle:** The reaction can be represented as

$$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{H}_2\text{O} \text{ (Main Reaction)}$$

$$\text{I}_2 + 2\text{S}_2\text{O}_3^- \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6 \text{ (Monitor Reaction)}$$

**Procedure:**

Place about 150ml of distilled water in a 500ml conical flask, and add about 20ml of 1M KI, 10ml of 2M H$_2$SO$_4$, and 1ml of starch solution into it. Add from the burette exactly 5ml 0.025M hypo solution. Keep it in a water bath to attain room temperature. Keep 0.1M H$_2$O$_2$ in another water bath.

Add 5ml of 0.1M H$_2$O$_2$ solution with a pipette and start the stop watch half way through the addition. Shake the solution and stand it in water bath. Note the time for appearance of blue colour. Repeat this procedure for 5 or 6 additions of hypo solution. Calculate the values of concentrations hydrogen peroxide (a-x) at the measured time intervals taking into account increase in volume of solution is due to additions of hypo solution. Concentration of H$^+$ ions and iodide ions also change but their initial values being high the proportionate change may be small and can be neglected. Initial concentration of hydrogen peroxide can be worked out in terms of equivalent volume of hypo solution. For this purpose measure out, 10ml of hydrogen peroxide solution, add carefully drop wise 10ml of concentrated sulphuric acid and 8gms of KI dissolved in minimum quantity of water. I$_2$ liberated is titrated against 0.025M hypo solution and tabulate the results. Volume of hypo added corresponding to time t.
\([H_2O_2]_0 \propto V_{\infty}[Vt = 0]\)

\([H_2O_2]_t \propto V_{\infty} - Vt\)

**Graph:**

Plot a graph by taking \(Vt\) vs time. A parabolic curve is obtained and slopes of the tangents to this curve at various times \(t\) represent the rate of reaction at these moments. Plot another graph \(\log(V_{\infty} - Vt)\) vs time. A straight line is obtained and the slope of this will be equal to the order of reaction.

**Result:**
Conductometry

1. Titration between a strong acid and strong base: Titration between HCl and NaOH

**Aim:** Determine the concentration of the given strong acid (HCl) solution by titrating it with standard strong base (NaOH) conductometrically.

**Apparatus:** Conductivity bridge, conductivity cell, 100 ml beaker, pipette, stand, etc.

**Chemicals:** HCl solution (≈ 0.1M), 0.5M NaOH solution.

**Principle:** The reaction between HCl and NaOH can be represented as:

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}
\]

HCl undergoes reaction with sodium hydroxide resulting in the formation of sodium chloride and unionized water. At the beginning of the titration the acid solution has a high conductivity due to highly mobile hydrogen ions. When NaOH is added to HCl solution the highly mobile H\(^+\) ions are replaced by less mobile sodium ions. This will result in the decrease of conductivity rapidly. At the end point the solution will contain only sodium and chloride ions. Hence there will be minimum conductivity. After the end point the conductivity rises due to the presence of fast moving OH\(^-\) ions. Thus the graph which is plotted between the conductance and the volume of sodium hydroxide added include two straight lines. The point of intersection of these two sharp lines gives the end point of the titration.

**Procedure:** Pipette out 40 ml of the given HCl solution into a clean 100 ml beaker and dip the conductivity cell in it. Connect the conductivity cell to a conductivity bridge and measure the initial conductance of the given HCl solution. Fill the burette with the given sodium hydroxide solution. Then add 0.5 ml of the given NaOH solution to the HCl solution present in the beaker and stir the contents well. Measure the conductance of the solution. Continue the addition of the sodium hydroxide solution in equal volumes (0.5 ml) until you get a minimum of 25-30 conductance readings. The end point of the titration can be detected by plotting a graph in between the measured conductance and the volume of sodium hydroxide that is added during the titration.
**Result:** The concentration of the given acid solution is ____________M.

**Observations**

<table>
<thead>
<tr>
<th>S. NO.</th>
<th>Volume of NaOH added (ml)</th>
<th>Conductance (mS)</th>
</tr>
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</table>

**CALCULATIONS:**

**HCl vs NaOH**

\[ M_1 V_1 = M_2 V_2 \]

- \( M_1 \) = Molarity of the given HCl solution
- \( V_1 \) = Volume of the HCl taken in the beaker
  - = 40 ml
- \( M_2 \) = Molarity of the given NaOH solution
  - = 0.5M
- \( V_2 \) = Volume of the NaOH required to neutralize the given acid
  - = end point volume

\[ M_1 = \frac{M_2 V_2}{V_1} \]
$$M_1 = 0.5 \times \text{E.P.V} / 40$$

End point of HCl
2. **Titration between a weak acid and strong base:**

**Titration between CH$_3$COOH and NaOH**

**Aim:** Determine the concentration of the given weak acid (CH$_3$COOH) solution by titrating it with standard strong base (NaOH) conductometrically.

**Apparatus:** Conductivity Bridge, conductivity cell, 100 ml beaker, pipette, stand, etc.

**Chemicals:** CH$_3$COOH solution ($\approx 0.1$ M), 0.5M NaOH solution.

**Principle:** The reaction between acetic acid and sodium hydroxide can be represented as:

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

At the beginning of the titration the conductance of the solution is found to be less because of poor dissociation of the acetic acid, which is a weak acid. Thus the number of ions produced by the dissociation of the acid is found to be less. When small amount of NaOH is added to the acetic acid solution the conductance increases due to the formation of sodium acetate which is a strong electrolyte than the acetic acid, hence dissociates rapidly producing more number of ions than acetic acid. At the end point of the titration both the sodium and acetate ions are present in the solution. The conductance of the solution increases when further sodium hydroxide is added to the solution at the end point. This increase is due to the presence of fast moving OH$^-$ ions.

**Procedure:** Pipette out 40 ml of the given CH$_3$COOH solution into a clean 100 ml beaker and dip the conductivity cell in it. Connect the conductivity cell to a conductivity bridge and measure the initial conductance of the given CH$_3$COOH solution. Fill the burette with the given sodium hydroxide solution. Then add 0.5 ml of the given NaOH solution to the CH$_3$COOH solution present in the beaker and stir the contents well. Measure the conductance of the solution. Continue the addition of the sodium hydroxide solution in equal volumes (0.5 ml) until you get a minimum of 25-30 conductance readings. The end point of the titration can be
detected by plotting a graph in between the measured conductance and the volume of sodium hydroxide that is added during the titration.

**Result:** The concentration of the given acetic acid solution is ____________M.

**Observations**

<table>
<thead>
<tr>
<th>S. NO.</th>
<th>Volume of NaOH added (ml)</th>
<th>Conductance (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CALCULATIONS:**

**CH₃COOH vs NaOH**

\[ M_1 V_1 = M_2 V_2 \]

\( M_1 = \text{Molarity of the given CH}_3\text{COOH solution} \)
\( V_1 = \text{Volume of the CH}_3\text{COOH taken in the beaker} \)
\( = 40 \text{ ml} \)
\( M_2 = \text{Molarity of the given NaOH solution} \)
\( = 0.5 \text{M} \)
\( V_2 = \text{Volume of the NaOH required to neutralize the given acid} \)
\( = \text{end point volume} \)

\[ M_1 = \frac{M_2 V_2}{V_1} \]

\[ M_1 = 0.5 \times \text{E.P.V} / 40 \]
3. DETERMINATION OF CELL CONSTANT

**Aim:** To determine the cell constant for a given cell at room temperature.

**Apparatus:** Beaker, Pipette, Standard flask-100ml, Weight box.

**Chemicals:** N/10 KCl Solution

**Principle:** Cell constant for a cell is defined as the constant factor which stands for the ratio of the specific conductance of a solution and its measured conductance in the cell.

Specific conductance / measured conductance = Cell constant

Or Specific conductance = measured conductance x Cell constant.

Since for any conductor the resistance \( R = \frac{1}{p} \frac{1}{a} \)

Taking reciprocals \( \frac{1}{R} = \frac{1}{p} \frac{a}{1} \)

Or \( \frac{1}{p} = \frac{1}{R} \frac{1}{a} \)

Therefore specific conductance = conductance x \( \frac{1}{a} \)

Therefore cell constant = \( \frac{1}{a} \)

**Procedure:** Prepare 0.1M KCl solution by weighing accurately 0.7455gm of KCl into a clean 100ml standard flask. From this 0.1M KCl solution prepare 100ml each of 0.05M, 0.02M, 0.01M, and 0.001M KCl solutions. Take about 40ml of each solution in to a clean and dry 100ml beaker and dip the conductivity cell and make necessary connections. Measure the conductance of each solution and note down.

Note the specific conductance values of each of the solution from literature. The Cell constant is calculated by using the formula given.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration</th>
<th>Observed conductance</th>
<th>Specific conductance</th>
<th>Cell constant</th>
</tr>
</thead>
</table>

**Result:** The cell constant was observed to be --------
4. Determination of dissociation constant of a weak acid

**Aim:** To determine the dissociation constants of acetic acid and to verify the Ostwald’s dilution law

**Apparatus:** Conductivity meter, Conductivity cell, Pipette, Glass rod, Beaker

**Chemicals required:** 0.1MCH₃COOH, distilled water

**Principle:** An acid dissociation constant, $K_a$, (also known as acidity constant, or acid-ionization constant) is a quantitative measure of the strength of an acid in solution. Each acid has a different $pK_a$. It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions. The larger the $K_a$ value, the more dissociation of the molecules in solution and thus the stronger the acid. Thus, a strong acid "wants" to get rid of its hydrogen ion, much more so than a weak acid. A small amount of strong acid in water will lead to a low pH whereas the same concentration of a weak acid will not lead to such a low pH.

Owing to the many orders of magnitude spanned by $K_a$ values, a logarithmic measure of the acid dissociation constant is more commonly used in practice. The logarithmic constant, $pK_a = -\log K_a$

$pK_a$ is sometimes also referred to as an acid dissociation constant. The larger the value of $pK_a$, the smaller the extent of dissociation at any given pH, the weaker the acid.

According to Arrhenius theory of electrolyte dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, law of mass action can be applied to such systems also.

The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution.

Weak electrolytes are partially dissociated in solution. Hence for such electrolytes the dissociation constant ($K_a$) is given by the Ostwald’s dilution law as follows
\[ K = \frac{C \alpha^2}{1 - \alpha} \]

Where \( C \) = the molar concentration, \( \alpha \) = degree of dissociation

The value of ‘\( \alpha \)’ is given as the ratio of the equivalent conductivity of the electrolyte at a particular concentration to that at infinite dilution. i.e. \( \alpha = \frac{\lambda_v}{\lambda_\infty} \).

However, in such cases \( \lambda_\infty \) may be determined by the application of Kohlrausch’s law of independent migration of ions and \( \lambda_v = 1000k_v/c \). [Where ‘\( k_v \)’ = specific conductance]

**Procedure:**

**Determination of cell constant:**

Take 40mL of 0.1M KCl solution into a 100mL beaker. Dip the conductivity cell into the KCl solution which in turn connected to the Conductivity Bridge and note down corresponding observed conductance value. Now take 40 mL0.01M KCl solution into the beaker and repeat the same experimental procedure as mentioned earlier. Calculate the cell constant using following formula

\[
\text{Cell constant} = \frac{\text{Specifi conductance}}{\text{Observed conductance}}
\]

<table>
<thead>
<tr>
<th>S. No</th>
<th>Concentration</th>
<th>Specific conductance ((k_v)) [From reference]</th>
<th>Observed conductance [From experiment]</th>
<th>Cell constant ((\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1M</td>
<td>12.88 mS/cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.01M</td>
<td>1.413 mS/cm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Take 40 mL 0.1M CH\(_3\)COOH solution in a clean beaker whose dissociation constant is to be determined. Now dip the conductivity cell whose cell constant is known which in turn connected to the Conductivity Bridge and note down corresponding conductance value. For other concentrations, remove the 20ml of
this solution and add 20ml distilled water to the same. Repeat the similar procedure for four more times and note down the corresponding conductance values for each dilution.

**Model graph:** Plot a graph between $\frac{\alpha^2}{1-\alpha}$ and $\frac{1}{c}$. The slope gives the dissociation constant of weak acid ($K_a$).

```
Model tabular form:

<table>
<thead>
<tr>
<th>Concentration (C)</th>
<th>Observed Conductance (mho)</th>
<th>Specific Conductance ($k_v$)</th>
<th>Equivalent Conductance $\lambda_v = \frac{1000 \times k_v}{c}$</th>
<th>Degree of dissociation $\alpha = \lambda_v / \lambda_\infty$</th>
<th>Dissociation constant ($K_a$)</th>
<th>$\frac{\alpha^2}{1-\alpha}$</th>
<th>$\frac{1}{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>0.0125</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.00625</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
```

**Result:** Dissociation constant of acetic acid ($K_a$) = ..................
4. Potentiometry

1. Titration of a strong acid with a strong base – Titration of HCl against NaOH

**Aim:** To find out the concentration of the given hydrochloric acid solution by potentiometric method.

**Apparatus:** Potentiometer, beaker (100 ml), stand, pipette, reference electrode (Calomel electrode), etc.

**Chemicals:** HCl solution, 0.1 M NaOH Solution, Quinhydrone powder, potassium chloride, etc.

**Principle:** The cell which is established to determine the concentration of an acid is represented as:

\[
\text{Hg(s), Hg}_2\text{Cl}_2 (s)|\text{KCl(sat)}||\text{H}^+ (c=?), Q, \text{H}_2\text{Q}|\text{Pt}
\]

The two electrodes are calomel electrode (reference electrode) and quinhydrone electrode which is a \(pH\) indicating electrode.

Quinhydrone is an equimolar mixture of both quinine and hydroquinone. This electrode is developed by the addition of a pinch of quinhydrone to a solution containing \(H^+\) ions to which it is reversible. During the titration as concentration of \(H^+\) ions changes the potential of the indicator electrode, quinhydrone electrode changes. This change in potential can be determined by coupling this with a reference electrode, calomel electrode whose potential value remains constant. Thus, the cell EMF varies only with the potential of indicator electrode. Thus, end point of such titration can be obtained by plotting a graph between the measured EMF and volume of base added which causes a change in potential of indicator electrode and hence the cell EMF.

**Procedure:** Pipette out 10 ml of the given HCl solution into a clean beaker and dip the calomel electrode and the Platinum electrode. Now a pinch of quinhydrone is added to the HCl solution. Connect the two electrodes to a potentiometer to read the cell EMF. Fill the burette with the given NaOH solution (0.1 M). Before the addition of sodium hydroxide to the acid solution measure the EMF. Now add 1 ml of the given sodium hydroxide solution to the HCl solution present in the beaker and stir with a glass rod and measure the EMF. Continue the addition of equal
volumes of base until a large change in EMF is observed. Now add 0.2 ml of NaOH every time to get an accurate end point. Continue this addition until you get a minimum of 7-8 readings after the end point.

Plot a graph between the measured EMF of the cell and volume of sodium hydroxide where in a sigmoid curve will be obtained. The inflexion of the curve i.e., where the curve changes its direction is taken as the end point of the titration.

Accurate endpoint can be obtained by plotting a graph between $\Delta E/\Delta V$ against $V_{avg}$.

**Result:** Concentration of the given HCl solution = _____________ M

<table>
<thead>
<tr>
<th>S. NO</th>
<th>Volume of NaOH added (ml)</th>
<th>EMF (mv)</th>
<th>$\Delta E$</th>
<th>$\Delta V$</th>
<th>$\Delta E / \Delta V$</th>
<th>$V_{avg}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Delta E / \Delta V$ Vs $V_{avg}$

$\Delta E / \Delta V \text{ Vs } V_{avg}$

**Table:**

<table>
<thead>
<tr>
<th>Volume of NaOH added (ml)</th>
<th>EMF (mv)</th>
<th>$\Delta E$</th>
<th>$\Delta V$</th>
<th>$\Delta E / \Delta V$</th>
<th>$V_{avg}$</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

$pH = 0.4595 - E_{cell} \over 0.0591$

EMF Vs Volume of NaOH

$\Delta E / \Delta V$ Vs $V_{avg}$

End point

Volume of NaOH added (ml)
CALCULATIONS:

**HCl Vs NaOH**

\[ M_1 V_1 = M_2 V_2 \]

- \( M_1 \) = Molarity of the sodium Hydroxide solution
  - \( = 0.1\text{M} \)
- \( V_1 \) = Volume of the NaOH required to neutralize the HCl solution
  - \( = \text{end point volume} \)
- \( M_2 \) = Molarity of the given HCl solution
- \( V_2 \) = Volume of the given HCl solution taken in the beaker = 10 ml
  \[ M_2 = \frac{M_1 V_1}{V_2} \]
  \[ M_2 = 0.1 \times \text{E.P.V} /10 \]
2. Titration of a Weak acid with a strong base – Titration of CH$_2$COOH against NaOH

**Aim:** To find out the concentration of the given acetic acid solution by potentiometric method.

**Apparatus:** Potentiometer, beaker (100 ml), stand, pipette, reference electrode, etc.

**Chemicals:** Acetic acid solution, 0.1 M NaOH Solution, Quinhydrone powder, potassium chloride, etc.

**Principle:** The cell which is established to determine the concentration of an acid is represented as:

\[
\text{Hg(s), Hg}_2\text{Cl}_2 (s)|\text{KCl(sat)}||\text{H}^+ (c=?), Q, H_2Q|\text{Pt}
\]

The two electrodes are calomel electrode (reference electrode) and quinhydrone electrode which is a pH indicating electrode.

Quinhydrone is an equimolar mixture of both quinine and hydroquinone. This electrode is developed by the addition of a pinch of quinhydrone to a solution containing H$^+$ ions to which it is reversible. During the titration as concentration of H$^+$ ions changes the potential of the indicator electrode, quinhydrone electrode changes. This change in potential can be determined by coupling this with a reference electrode, calomel electrode whose potential value remains constant. Thus, the cell EMF varies only with the potential of indicator electrode. Thus, end point of such titration can be obtained by plotting a graph between the measured EMF and volume of base added which causes a change in potential of indicator electrode and hence the cell EMF.

**Procedure:** Pipette out 10 ml of the given acetic acid solution into a clean beaker and dip the calomel electrode and the Platinum electrode. Now a pinch of quinhydrone is added to the acetic acid solution. Connect the two electrodes to a potentiometer to read the cell EMF. Fill the burette with the given NaOH solution (0.1 M). Before the addition of sodium hydroxide to the acid solution measure the EMF. Now add 1 ml of the given sodium hydroxide solution to the acetic acid solution present in the beaker and stir with a glass rod and measure the EMF. Continue the addition of equal volumes of base until a large change in EMF is
observed. Now add 0.2 ml of NaOH every time to get an accurate end point. Continue this addition until you get a minimum of 7-8 readings after the end point.

Plot a graph between the measured EMF of the cell and volume of sodium hydroxide where in a sigmoid curve will be obtained. The inflexion of the curve i.e, where the curve changes its direction is taken as the end point of the titration.

Accurate endpoint can be obtained by plotting a graph between $\Delta E/\Delta V$ against $V_{avg}$.

**Result:** Concentration of the given acetic acid solution = _____________ M.

<table>
<thead>
<tr>
<th>S. NO</th>
<th>Volume of NaOH added (ml)</th>
<th>EMF (mv)</th>
<th>$\Delta E$</th>
<th>$\Delta V$</th>
<th>$\Delta E / \Delta V$</th>
<th>$V_{avg}$</th>
</tr>
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<tbody>
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</tr>
</tbody>
</table>

$\text{pH} = 0.4595 - E_{\text{cell}}$

\[
0.0591
\]
CALCULATIONS:

\[ \text{CH}_3\text{COOH Vs NaOH} \]

M_1 = Molarity of the sodium Hydroxide solution \( = 0.1 \text{M} \)

V_1 = Volume of the NaOH required to neutralize the HCl solution
\( = \) end point volume

M_2 = Molarity of the given acetic acid solution

V_2 = Volume of the given acetic acid solution taken in the beaker \( = 10 \text{ ml} \)

\[ M_2 = \frac{M_1 V_1}{V_2} \]

\[ M_2 = 0.1 \times \text{E.P.V} /10 \]
In case of a weak acid, the dissociation constant can be determined by using Henderson’s equation. According to this equation,

$$pH = pKa + \log \frac{[\text{salt}]}{[\text{acid}]}$$

At Half neutralisation point, \(pH = pKa\)

Thus, above equation reduces to

\(pH = pKa\)

and from \(pKa\) value \(Ka\) (dissociation constant) can be calculated.

\(pKa = -\log Ka\)
3. **Weak acid vs Strong base (Acid-Base Titration)**

**Aim:** To find the strength of acetic acid by titrating it against sodium hydroxide potentiometrically and also calculate the dissociation constant \( K_a \) of the acid using quinhydrone electrode.

**Apparatus:** Potentiometer, calomel electrode, Pt wire, salt bridge, beakers

**Chemicals:** 0.1M AcOH, 0.1M NaOH, saturated KCl, Quinhydrone etc.

**Principle:** Potentiometric methods of analysis are based upon measurements of the potential of electrochemical cells under conditions of zero current, where the Nernst equation governs the operation of potentiometry. A typical cell for potentiometric analysis consists of a reference electrode, an indicator electrode and a salt bridge.

To measure the potential changes, the indicator electrode is coupled with a reference electrode using a salt bridge. The cell can be depicted as follows

\[
\text{Hg (l), Hg}_2\text{Cl}_2(\text{s}) \mid \text{KCl} \parallel \text{H}^+, \text{Q}, \text{QH}_2 \mid \text{Pt}
\]

Quinhydrone is an equimolar mixture of quinone and hydroquinone. In an aqueous solution of quinhydrone, the following reversible reaction takes place

\[
\text{Q}^{\Delta} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{QH}_2
\]

Because the above reversible reaction involves \( \text{H}^+ \) ions, the quinhydrone in solution function as redox electrode in contact with an inert conductor such as platinum. The potential of the quinhydrone electrode is sensitive to the pH of the solution.

The EMF of the cell is given as

\[
E_{\text{Cell}} = E_Q - E_{\text{SCE}}
\]
\[ E_Q = E^0_Q - (2.303RT/F) \log (1/H^+) \]
\[ E_{\text{Cell}} = E^0_Q - (2.303RT/F) \log (1/H^+) - 0.242 \]
\[ E_{\text{Cell}} = E^0_Q - (2.303RT/F) \text{pH} - 0.242 \]
\[ E_{\text{Cell}} = 0.699 + 0.0591 \log (H^+) - 0.242 \]
\[ E_{\text{Cell}} = 0.457 + 0.0591 \log (H^+) \text{ (or) } E_{\text{Cell}} = 0.457 - 0.0591 \text{pH} \]

As the titration proceeds, H\(^+\) ion concentration decreases and hence EMF of the cell decreases slowly but in the vicinity of the equivalence point the rate of change of potential is very rapid or maximum. On crossing the equivalence point, again EMF changes in small decrements. From the sharp break in the curve, equivalence point can be determined, from which the strength of the acid can be calculated.

**Determination of dissociation constant of weak acid:**

The Henderson-Hasselbalch equation is

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{salt}]}{[\text{acid}]} \right) \]

At half neutralization point, the concentrations of the salt and acid are equal,

Then \( \log \left( \frac{[\text{salt}]}{[\text{acid}]} \right) = 1; \quad \text{pH} = \text{pK}_a \)

\[ \frac{(0.457 - E_{\text{cell}})}{0.0591} = pK_a \]

\[ K_a = \text{antilog} \left( \frac{(0.457 - E_{\text{cell}})}{0.0591} \right) \]

**Procedure:** Take 20 mL of 0.1M AcOH in a clean 100 mL beaker and add sufficient amount of distilled water (30 mL) so that the electrodes are completely dipped. Add a pinch of quinhydrone to saturate the solution and dip indicator (working) electrode in the solution. Combine the Pt electrode (contact electrode) with the calomel electrode through a salt bridge. The two electrodes are connected to the potentiometer. Once the potentiometer is standardized, add 1mL of 0.1M NaOH from the micro burette to acetic acid solution taken in a beaker. Stir the solution carefully and note down the corresponding EMF value. Continue the
addition of NaOH solution from the burette and note the EMF and tabulate the data.

Model Tabular Form:

<table>
<thead>
<tr>
<th>S. No</th>
<th>Volume of NaOH (mL)</th>
<th>EMF (mv)</th>
<th>ΔE (mv)</th>
<th>ΔV (mL)</th>
<th>ΔE/ΔV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
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</tr>
<tr>
<td>6</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Graphs:

1) Plot a graph between EMF and volume of NaOH. This gives an equivalence point (sigmoid).

2) Plot a graph between ΔE/ΔV and volume of NaOH. A differential graph is obtained.
**Result:** The end point for the titration of 20mL AcOH against 0.1M NaOH is ............. mL

Strength/Concentration of given AcOH solution is ......... M

Dissociation constant \(K_a\) for weak acid = ..................
4. DETERMINATION OF SINGLE ELECTRODE POTENTIAL

**Aim:** To determine the single (standard) electrode potential of silver electrode Potentiometrically

**Apparatus:** Potentiometer, calomel electrode, silver electrode, salt bridge, beaker

**Chemicals required:** 0.1M AgNO₃, saturated KCl etc.

**Principle:** To measure changes, the indicator electrode is coupled with a reference electrode using a salt bridge. The potential of reference electrode remains unchanged during the progress of reaction. The cell set up is as follows

\[
\text{Hg (l), Hg}_2\text{Cl}_2(\text{s}) | \text{KCl} || \text{Ag}^+/\text{Ag} \\
E_{\text{Ag}} = E^0_{\text{Ag}} - (2.303RT/ F) \log (1/\text{Ag}^+) \\
E_{\text{Cell}} = E_{\text{Ag}} - E_{\text{SCE}} \\
E_{\text{Ag}} = E^0_{\text{Ag}} - (2.303RT/ F) \log (1/\text{Ag}^+) \\
E_{\text{Cell}} = E^0_{\text{Ag}} + 0.0591 \log (\text{Ag}^+) - 0.242 \\
E^0_{\text{Ag}} = E_{\text{Cell}} + 0.0591 \log (\text{Ag}^+) + 0.242
\]

**Procedure:** Take 20ml of 0.1M AgNO₃ into a 100ml beaker. Dip the Ag electrode in the beaker and connect it to the Potentiometer. Measure the potential difference of the solution. Remove 10ml of solution from the beaker and add 10ml of distilled water such that the solution is diluted to M/20. Now record the EMF value of the cell. Repeat the process with various concentration of AgNO₃ say M/40, M/80, M/160. \(E^0_{\text{Ag}}\) can be calculated using Nernst equation.

**Model tabular form:**
<table>
<thead>
<tr>
<th>S. No</th>
<th>Conc. of AgNO₃</th>
<th>E₉ₑₐₜ (Volts)</th>
<th>log [Ag⁺]</th>
<th>E⁰_Ag = E₉ₑₐₜ - 0.0591 log [Ag⁺] + 0.242</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.05M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.025M</td>
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</tr>
<tr>
<td>4</td>
<td>0.0125M</td>
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</tr>
<tr>
<td>5</td>
<td>0.00625M</td>
<td></td>
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</tbody>
</table>

**Graph:** Plot a graph between E₉ₑₐₜ (EMF) and log [Ag⁺]. Intercept is equal to E⁰_Ag – 0.242. From this E⁰_Ag can be determined

Result:

E⁰_Ag (From graph) =...... Volts

E⁰_Ag (From Calculations) =...... Volts
5. Polarimetry

1. Determination of Specific rotation of Sucrose

**Aim:** To determine the specific rotation of cane sugar (sucrose).

**Apparatus:** Polarimeter, sodium lamp, Polarimeter tube, standard flasks, simple balance, pipette, etc.

**Chemicals:** 20% Sucrose solution.

**Principle:** Specific rotation can be defined as the angle of rotation when polarized light is passed through one decimeter of the solution having concentration of 1g/1ml. It is represented by \( [\alpha] \).

\[
[\alpha] = \frac{\theta}{lc}
\]

Where \( \theta = \text{angle of rotation} \)

\( l = \text{length in decimeters} \)

\( c = \text{Concentration of the solution} \)

When ‘c’ is expressed in %, then

\[
[\alpha] = \frac{\theta \times 100}{lc}
\]

When \( l = 2 \) decimeters then,

\[
[\alpha] = \frac{\theta \times 50}{c}
\]

On rearranging,

\[\theta = c \times \frac{\alpha}{50}\]

Thus, when a graph is plotted between angle of rotation and concentration a straight line passing from the origin is obtained. From the slope of the straight line specific rotation can be evaluated.

**Procedure:** Calibration of the polarimeter tube
Set up a sodium vapour lamp and adjust the height of the lamp and the optical axis of the instrument for maximum illumination of the polarizer. Take a properly
cleaned polarimeter tube and fill it with distilled water. Avoid entry of air bubbles into the tube. There should be no liquid drops on the outside of the glass plate. Place the tube between the polarizer and analyzer and determine the zero point of the polarimeter by rotating the analyser until two halves of the field of view are equally dark.

By weighing 20 grams of sucrose and dissolving in 100ml of water in a clean standard flask results in 20% sucrose solution. The obtained solution is filled in the polarimeter tube and the angle of rotation of 20% sucrose solution is measured. The experiment is repeated with 15%, 10%, 5% and 2.5% concentrations of sucrose solution.

A graph is plotted between θ and % of sucrose solution. A straight line is obtained. From the slope specific rotation can be obtained.

**Result:** The specific rotation of sucrose is ........................deg.dm⁻¹g⁻¹cm³

<table>
<thead>
<tr>
<th>S. No.</th>
<th>% of sucrose solution</th>
<th>θ (Angle of rotation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Slope = α/50

α = slope x 50
2. Acid-catalyzed hydrolysis of sucrose (Inversion of sucrose)

**Aim:** To study acid catalysed inversion of sucrose at different concentrations of acid and determination of rate constants at different concentrations of the acid.

**Apparatus:** Polarimeter, Sodium lamp, polarimeter tube, beakers, stand, pipette, etc.

**Chemicals:** 20% sucrose solution, Std. HCl solution

**Principle:** Hydrolysis of sucrose in the presence of an acid is an example of Pseudo-first order reaction. It can be represented as:

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_{6}\text{H}_{12}\text{O}_6 + \text{C}_{6}\text{H}_{12}\text{O}_6
\]

(Sucrose) (Glucose) (Fructose)

The rate equation, \(k\) can be represented as

\[
k = \frac{2.303}{t} \log \frac{a}{(a-x)}
\]

In terms of angle of rotation,

\[
k = \frac{2.303}{t} \log \frac{\theta o - \theta a}{\theta t - \theta a}
\]

Where \(\theta o\) = angle of rotation at \(t=0\) (is a measure of initial concentration of the reactant)

\(\theta t\) = angle of rotation at \(t=t\) (is a measure of concentration of the reactant at different time intervals)

\(\theta a\) = angle of rotation at infinite time

The above reaction is also called as acid catalysed Inversion of sucrose because during the reaction the dextrorotatory sucrose undergoes change in its optical rotation and forms leavo rotator fructose and dextrorotatory glucose. Since leavo compound is large it is found that sucrose undergoes inversion and forms a leavo compound.

The reaction can be studied by measuring the change in optical rotation of sucrose at different time intervals since sucrose is an optically active compound.
**Procedure:** To 50 ml of 20% sucrose add 50ml of 2M HCl and shake the contents for a while and fill the polarimeter tube with this reaction mixture and insert the tube in the polarimeter (an instrument used for measuring angle of rotation of plane polarized light). Immediately read the angle of rotation and note down the reading \( \theta_t \). Again the rotation is noted at particular time intervals (i.e. 5, 10,15,20…..).Lastly the solution is heated up to 40ºC and is again filled in the polarimeter tube to get \( \theta_a \) value. Plot a graph between \( \log (\theta_t - \theta_a) \) against time, \( t \) where a straight line is obtained. From the slope of the straight line ‘\( k \)’ can be evaluated.

**Result:** Rate Constant, \( k_1 = \) _____________min\(^{-1}\) at 1M HCl.
Rate Constant, \( k_2 = \) _____________min\(^{-1}\) at 2M HCl.

**Observations:**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Time (min)</th>
<th>( \theta_t )</th>
<th>( \frac{\theta_t - \theta_a}{\theta_a} )</th>
<th>Log ( \frac{\theta_0 - \theta_a}{\theta_t - \theta_a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ \log \theta - t = \frac{k}{2.303} \]
**Adsorption of acetic acid on animal charcoal.**

**Aim:** To verify the adsorption isotherm for acetic acid adsorption on animal charcoal.

**Apparatus:** Reagent bottles-5, burette, funnel, watmann paper no. 41, pipette, conical flask.

**Chemicals:** 0.1N acetic acid, 0.1N NaOH, charcoal 1gm, phenolphthalein.

**Principle:** Freundlich proposed a relation between the amount of solute adsorbed on a definite amount adsorbent and the equilibrium concentration of the adsorbate in the solution. According to which

\[
\frac{x}{m} = kC_e^{1/n} \Rightarrow \log(\frac{x}{m}) = \log k + \frac{1}{n} \log C_e
\]

where \( x \) = amount of solute adsorbed;
\( m \) = mass of the adsorbent
\( C_e \) = equilibrium concentration of adsorbate; \( k \) = constant.

\( n \) = no. of layers of acetic acid adsorbed to the surface layer of charcoal.

**Procedure:** Take 5 clean reagent and number them 1-5. Prepare the following soln.mixtures.
<table>
<thead>
<tr>
<th>Bottle no.</th>
<th>Volume of acetic acid</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50ml</td>
<td>0ml</td>
</tr>
<tr>
<td>2</td>
<td>40ml</td>
<td>10ml</td>
</tr>
<tr>
<td>3</td>
<td>30ml</td>
<td>20ml</td>
</tr>
<tr>
<td>4</td>
<td>20ml</td>
<td>30ml</td>
</tr>
<tr>
<td>5</td>
<td>10ml</td>
<td>40ml</td>
</tr>
</tbody>
</table>

(1) Stopper each bottle after adding 1gm of charcoal and shake the bottles in a rotatory motion and allow them to stand for at least 1 hour.

(2) Fill the burette with 0.1N NaOH solution. Pipette out 10ml of stock 0.1M acetic acid solution into a clean conical flask and add 1 or 2 drops of phenolphthalein indicator and titrate it against sodium hydroxide solution. The end point is noted when a faint pink colour is observed.

(3) After 1 hour filter the contents of each bottle separately through a watmann filter paper no. 41. While filtering reject the first 5ml of the filtrate and collect the rest. Wait until the filtration is complete and pipette out 10ml of the filtrate in to a clean conical flask and titrate it against with 0.1N NaOH by adding 1-2 drops of phenolphthalein indicator. The end point is noted when a faint pink colour is observed.

(4) Repeat the procedure with the filtrate of other bottles and tabulate the results.
Table 2

<table>
<thead>
<tr>
<th>Bottle No.</th>
<th>Initial conc($C_i$)</th>
<th>Volume of N/10 NaOH($C_e$)</th>
<th>$x = (C_i - C_e)/2$</th>
<th>log($x/m$)</th>
<th>log($C_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
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<tr>
<td>3</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Fig 5.

Graph: A graph (similar to fig.5) is plotted by taking log($x/m$) on y-axis and log($C_e$) on x-axis. A straight line cutting y-axis is obtained. The slope of the straight line is equal to $1/n$ and the intercept is equal to log($k$).

Result: The Freundlich adsorption isotherm is verified.
Study of effect of added electrolyte on CST of phenol water system.

**Aim:** To study of effect of added electrolyte on CST of phenol water system.

**Apparatus:** Boiling tube, beaker, two holed rubber cork thermometer, wire stirrer.

**Chemicals:** Phenol, 1% NaCl, distilled water.

**Principle:** Certain mixtures are partially miscible and are soluble in each other only under certain conditions. When the temperature is altered at constant pressure the initially partially miscible mixture become completely miscible and the temp at which they become completely miscible is known as CST. The CST of a solution is specific and is sensitive to the impurities.

If an impurity is soluble only in one of the components it alters the CST of the system. Addition of impurities to the phenol water system raises the CST of the system. The change in CST is found to be linearly proportioned to the % of impurity.

**Procedure:** Prepare 100ml of 1% NaCl solution. Fix the thermometer and wire stirrer into the two holed rubber stopper. Now prepare the following compositions.

<table>
<thead>
<tr>
<th>Vol of Phenol</th>
<th>5</th>
<th>5</th>
<th>5</th>
<th>5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol of 1%NaCl</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Vol of H₂O</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

The above compositions are taken in a boiling tube which is stoppered with rubber cork containing thermometer and wire stirrer. The boiling tube is placed in a beaker containing water. Increase the temperature of the system by heating it. Stir the mixture constantly with the help of wire stirrer and it appears to be cloudy. The liquid mixture is heated until the last trace of cloudiness disappears. The temperature of the system is noted as heating temperature \(T_1^\circ C\). Now immediately remove the burner and allow it to cool and the temperature at which the cloudiness...
reappears is noted as cooling temperature as \(T_2^\circ{\text{c}}\) and the mean of the two temperatures is noted.

The above procedure is repeated for all the other compositions and these heating and cooling temperatures are noted.

**Graph:** Plot a graph between the percentage of salt in solution on x-axis and its miscibility temperature on y-axis. A straight line passing through origin is obtained.

**Result:** Using this unknown conc. of the electrolyte can be obtained.
**Determination of CST of solution**

**Aim:** To determine the critical solution temperature of the phenol water system.

**Apparatus:** Boiling tube, beaker, wire stirrer thermometer, two holed rubber cork, graduated pipettes.

**Principle:** Certain solution mixtures are partially miscible. The partially miscible liquid pairs are soluble in each other only up to certain limits. On addition of small quantity of either of the liquid increases the relative immiscibility beyond a certain temperature the two liquids are completely miscible. This temperature at which the two partially miscible liquids become completely miscible is known as critical solution temperature.

**Procedure:** Take a clean beaker filled with tap water place it on the bunsen burner. Place the thermometer and wire stirrer into the boiling tube using a two holed rubber stopper. Now prepare the following mixtures.

<table>
<thead>
<tr>
<th>Vol. of phenol</th>
<th>9ml</th>
<th>8ml</th>
<th>7ml</th>
<th>6ml</th>
<th>5ml</th>
<th>4ml</th>
<th>3ml</th>
<th>2ml</th>
<th>1ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. of water</td>
<td>1ml</td>
<td>2ml</td>
<td>3ml</td>
<td>4ml</td>
<td>5ml</td>
<td>6ml</td>
<td>7ml</td>
<td>8ml</td>
<td>9ml</td>
</tr>
</tbody>
</table>

The above compositions are taken in a boiling tube which is stoppered with rubber cork containing thermometer and wire stirrer. The boiling tube is placed in the beaker containing water. The temperature of the system is increased by heating the water bath. The liquid mixture is constantly stirred with the help of wire and the liquid mixture appears to be cloud. The liquid mixture is heated until the last trace of cloudiness disappears. The temperatures of the mixture is noted as heating temperature ($T_1 ^{\circ}C$) and immediately remove the burner and allow it to cool and the temperature at which the cloudiness just appears is also noted as ($T_2 ^{\circ}C$).

The above procedure is repeated for all the other compositions and their heating and cooling temperatures are noted.

**Graph:** Plot a graph by taking composition of phenol on x-axis and mean of the temperatures on y-axis. A parabolic curve is obtained. The value of maximum
point on x-axis gives the composition and that on y-axis gives the temperature at which the two liquid mixtures remain completely miscible.

Result:
- GST of phenol in water = 65°C
- Composition of phenol =

Precaution:
The volume of the solution should be taken in such a way that the bulb of the thermometer is completely dipped into the mixture.
Semester-II

1. Distribution:

**DISTRIBUTION OF I$_2$ BETWEEN CCl$_4$ AND aq KI**

**Aim:** To determine the equilibrium constant and determine the unknown concentration of given KI by following the distribution of I$_2$ between CCl$_4$ and aq KI.

**Apparatus:** Five Reagent bottles, Burette, Pipettes, Conical flasks & measuring jar

**Chemicals:** Saturated I$_2$/CCl$_4$, aq KI (0.25M), M/20 Hypo, Starch indicator

**Principle:** I$_2$ distributes itself between CCl$_4$ and aq KI. The solubility of I$_2$ is due to formation of KI$_3$ complex, the solubility of I$_2$ increases with increase in concentration of KI. The partition study experiment can be used to get the equilibrium constant.

\[
\text{KI} + \text{I}_2 \xrightleftharpoons{K} \text{KI}_3
\]

According to law of mass action equilibrium constant,

\[
K = \frac{[\text{KI}_3]}{[\text{KI}][\text{I}_2]}
\]

Where, [KI$_3$], [KI] and [I$_2$] represent the equilibrium concentrations. From previous experiment, we have,

\[
K_D = \frac{C_{aq}}{C_{org}}
\]

Where $C_{org}$ and $C_{aq}$ are concentrations of I$_2$ in organic and aqueous layers respectively.

\[
C_{aq} = \frac{C_{org}}{K_D}
\]

Total concentration of I$_2$ in aqueous layer represented as $C_1$

Since KI combines with equivalent amount of I$_2$ to form KI$_3$ complex

Concentration of free I$_2$ in aqueous layer = $C_2$
Concentration of KI\textsubscript{3} = C\textsubscript{1} - C\textsubscript{2} (Combined concentration of I\textsubscript{2})

Initial concentration of KI = C\textsubscript{3}

By knowing the values of [KI\textsubscript{3}], [KI] and [I\textsubscript{2}] equilibrium constant can be evaluated as follows

\[ K = \frac{(C_1-C_2)}{C_3 \times C_1} \]

**Procedure**: Take five reagent bottles and prepare following solution mixtures.

<table>
<thead>
<tr>
<th>S. No</th>
<th>I\textsubscript{2} in CCl\textsubscript{4} (mL)</th>
<th>Aq KI (mL)</th>
<th>H\textsubscript{2}O (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

Now stopper the bottles and shake each bottle for 15 min. Then keep aside. Allow the reagent bottle for the layers to separate. Meanwhile fill the burette with M/20 Hypo. Now pipette out 10mlof Organic (lower) & Aqueous (upper) layers into two conical flasks separately. Titrate both the layers against M/20 Hypo solution by adding 2-3 drops of Starch indicator. Note down the readings as V\textsubscript{org} & V\textsubscript{aq} respectively. Same experimental procedure is repeated for other reagent bottles

**Model graph**: Plot a graph between C\textsubscript{aq}/C\textsubscript{org} and concentration of KI, straight line with positive slope is obtained.
Model tabular form:

<table>
<thead>
<tr>
<th>Reagent bottle</th>
<th>( V_{\text{org}} )</th>
<th>( V_{\text{aq}} )</th>
<th>( C_{\text{org}} )</th>
<th>( C_{\text{aq}} )</th>
<th>( C_{\text{aq}} / C_{\text{org}} )</th>
<th>[KI]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Unknown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Result:** Concentration of given KI (Unknown) solution = ............
CHEMICAL KINETICS

1. STOICHIOMETRY OF PERSULPHATE - IODIDE REACTION

Aim: To determine stoichiometry of persulphate - iodide reaction

Apparatus: Iodination flask, burette, pipette

Chemicals required: Distilled water, M/10 KI solution, M/20 K₂S₂O₈ solution, starch indicator, M/200 hypo solution

Principle: The quantitative relationship existing between the quantities of the reactants and the products in a chemical reaction is termed as stoichiometry. The balanced chemical equation gives the stoichiometry of reactants reacted to give products.

\[ \text{K}_2\text{S}_2\text{O}_8 + 2\text{KI} \rightarrow 2\text{K}_2\text{SO}_4 + \text{I}_2 \]
\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

Here to know the stoichiometry or the relative ratio in which K₂S₂O₈ and KI reacts, the iodine liberated when a definite quantity of potassium persulphate is allowed to react with excess of KI solution can be estimated by titrating it against standard hypo using starch indicator.

Procedure: Weigh exactly 0.5gm of K₂S₂O₈ and transfer it into 100ml standard flask and make up the solution up to the mark. Now transfer whole solution into an iodination flask. To it, add 2gm KI. Shake thoroughly. Close the lid and keep it in the dark for one hour.

Pipette out 10ml of above reaction mixture and titrate with standard M/200 hypo solution using starch as an indicator. Repeat the titration for concurrent readings. In case the readings differ by a large volume; allow the reaction mixture to stay in the dark for 1 hour for complete reaction. From the volume of hypo consumed, calculate the number of moles of iodine liberated and hence the number of moles of iodine reacted with potassium persulphate.

Model tabular form:
<table>
<thead>
<tr>
<th>S.No</th>
<th>Volume of reaction mixture (mL)</th>
<th>Burette reading (mL)</th>
<th>Volume of hypo (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>initial</td>
<td>final</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Result:**

From the experimental observations, the number of moles of iodine reacted with 1 gram of potassium persulphate = 

Thus, the ratio of moles of persulphate to the number of moles of iodine is =
2. Determination of order of the reaction with respect to KI by isolation method

**Aim:** Determination of order with respect to [I] by isolation method

**Apparatus:** Iodination flask, Beaker, pipette, burette, stop watch

**Chemicals required:** M/4 KI, M/40 K₂S₂O₈, M/4 KCl, M/200 Hypo, starch indicator

**Principle:** The order of reaction with respect to KI can be obtained by Ostwald dilution method. According to this, the experiment is performed by taking all reactants, except one, in excess. The reactant which is not taken in excess is said to be isolated and order with respect to the isolated reactant can be determined. The reaction can be followed by titrating the liberated iodine against hypo solution at different time intervals. The titre values are proportional to the amount of iodine liberated in the course of time. The reaction between liberated iodine and hypo and is represented by the following reaction:

\[
K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2
\]

\[
2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI
\]

**Procedure:** Prepare two sets of solutions

**Set-1:**

Take 50ml of M/4 KI solution in an iodination flask and add 50ml of M/40 potassium persulphate solution to the same flask. Immediately start stop watch. After 5 minutes pipette out 10ml of reaction mixture into a conical flask containing ice-cold water and 1-2 ml starch indicator. Titrate this solution against M/200 Hypo solution and note down the end point at first disappearance of blue color. And repeat the similar procedure and determine \( V_t \) corresponding to the times 10, 15, 20 …. minutes respectively.

**For \( V_\infty \) value:** At the early stage of the reaction i.e., after 2 to 3 minutes, pipette out 10ml of the reaction mixture into a clean conical flask and add excess of KI to it (one spatula of solid KI) cover it with watch glass and keep it in dark for about 30 minutes. After 30 minutes take out the flask and wash the lid of watch glass into
the conical flask. Titrate the contents of the conical flask against hypo and note down the reading as $V_\infty$.

**Set-2:**

Take 25ml of M/4 KI solution in an iodination flask; add 25ml of M/4 KCl and 50ml of M/40 K$_2$S$_2$O$_8$ to it. Repeat the same procedure as described for the set-1. Tabulate the titre values.

**Model tabular form:**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Volume of hypo (ml)</th>
<th>$(V_\infty - V_t)$</th>
<th>$\log(V_\infty - V_t)$</th>
<th>$\log \left( \frac{V_\infty}{V_\infty - V_t} \right)$</th>
<th>$\log \left( \frac{V_\infty}{V_\infty - V_t} \right)$</th>
<th>$k = \frac{2.303}{t} \log \left( \frac{V_\infty}{V_\infty - V_t} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
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<td>15</td>
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<td>25</td>
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<tr>
<td>30</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td></td>
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</tr>
</tbody>
</table>

**Model graph: (For two sets)**

Plot a graph between $\log \left( \frac{V_\infty}{V_\infty - V_t} \right)$ Vs time, straight line passing through origin is obtained. The slope of the line gives rate constant.

Plot another graph between $\log (V_\infty - V_t)$ Vs time, a straight line with negative slope is obtained.
Result:

From calculations,

Set-I, Rate constant, \( k_1 \) = \\
Set-II, Rate constant, \( k_2 \) = \\
\( k_1 : k_2 \) = 

From graph-1, Rate constant \( k_1 \) =

Rate constant \( k_2 \) =
\( k_1 : k_2 \) = 

From graph-2, Rate constant \( k_1 \) =

Rate constant \( k_2 \) =
\( k_1 : k_2 \) = 

slope = \( \frac{k}{2.303} \)
3. Determination of order of the reaction with respect to K$_2$S$_2$O$_8$ by initial rate method

**Aim:** To determine the order of the reaction with respect to K$_2$S$_2$O$_8$ by initial rate method by following the kinetics of Persulphate-iodide reaction

**Apparatus:** Iodination flask, burette, pipette, standard flask, conical flask, beaker, beaker, measuring jar, stop watch etc.

**Chemicals required:** 0.1M KI, 0.05M K$_2$S$_2$O$_8$, 0.05M K$_2$SO$_4$, M/200 hypo, starch indicator.

**Principle:**

**Chemical reaction:**

\[ S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-} \]

\[ 2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \quad \text{(Sodium tetra thionate)} \]

The rate law for the above reaction is expressed as,

\[ \text{Rate} = k \ [I^-]^m \ [S_2O_8^{2-}]^n \]

The rate of a chemical reaction is a measure of how quickly reactants are consumed or products are formed during a chemical reaction. The rate is the change in reactant or product concentration divided by the change in time. The rate depends upon several factors, including the concentrations of the reactants (and sometimes catalysts). Since reactant concentrations decrease as the reaction proceeds, reaction rates also decrease as the reaction proceeds—that is, the reaction rate does not remain constant during the reaction. The reaction rate will be different depending upon which time interval we consider. Note that the rate is greatest at the beginning of the reaction and is very low towards the end. Several different types of reaction rates can be measured. The average rate is the change in reactant or product concentration divided by the change in time. The larger the period of time over which an average rate is measured, the more the rate changes over that time period. Thus, it is common to make the time period as short as possible. The shorter the time period, the less the rate will change during that period. If the time period is made infinitesimally short, then the rate is called an instantaneous rate. The instantaneous rate at the very beginning of the reaction when time = 0 is called the initial rate.
In this experiment, concentration of KI remains constant

Thus, the order ‘n’ can be determined by altering the initial concentration of Persulphate and observing the rate. The rate expression is thus modified as,

\[
\text{Rate} = k [S_{2}O_{8}^{2-}]^n
\]

\[
\log (\text{rate}) = \log k + n \log [S_{2}O_{8}^{2-}]
\]

**Procedure:** Prepare 0.1M KI, 0.05M \(K_2S_2O_8\), 0.05M \(K_2SO_4\) and M/200 hypo and prepare the following sets of mixtures

**Table: Sets for the determination of order with respect to \(K_2S_2O_8\) by initial rate method:**

<table>
<thead>
<tr>
<th>Sets</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of KI (mL)</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Volume of (K_2S_2O_8) (mL)</td>
<td>50</td>
<td>40</td>
<td>30</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Volume of (K_2SO_4) (mL)</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>

Pipette out 10ml of the reaction mixture after 5 min from the first set and pour into the conical flask, already containing few pieces of ice and some ice cold water. Add few drops of starch indicator to it. Note the time and titrate against the hypo filled in the burette. Repeat the same process for 10, 15, 20 … minutes and note down the burette readings at above mentioned regular intervals. And repeat the similar experimental procedure for all the sets given in the tabular form. Calculate the concentration of \(K_2S_2O_8\) in the reaction mixture from each set.

**Model graph:** Plot a graph between volumes of hypo (mL) required Vs time (min)for each set separately, it gives a curve or straight line, the slope of the line gives the rate for the reaction. Plot another graph between log [Rate] Vs log \([K_2S_2O_8]\). The slope of this graph gives the order of the reaction.
**Result:** Order of the reaction between K$_2$S$_2$O$_8$ - KI with respect to K$_2$S$_2$O$_8$ by initial rate method

**Model tabular form:**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Time (min)</th>
<th>Volume of hypo required (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td></td>
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<tr>
<td>5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Set</td>
<td>$[S_2O_8^{2-}]$</td>
<td>Rate</td>
</tr>
<tr>
<td>-----</td>
<td>----------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td></td>
<td></td>
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<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conductometry:

1. TITRATION OF MIXTURE OF STRONG AND WEAK ACID VS STRONG BASE

Aim: To determine the strengths of strong (HCl) and weak acid (AcOH) in a given mixture conductometrically

Apparatus: Conductivity Bridge, Conductivity cell, beaker, Pipette, Micro burette, Glass rod

Chemicals required: 0.1M HCl, 0.1M CH₃COOH, 0.5M NaOH

Principle: Conductometric titration is a type of titration in which the electrolytic/ionic conductivity of the solution continuously monitored as one reactant is added. The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The main advantages to the conductometric titration are its applicability to very dilute, homogeneous suspension, coloured solutions and to system that involve relative incomplete reactions, which cannot be used with normal indicators.

The conductance method can be employed to follow the course of a titration, provided that there is a significant difference in conductance between the original solution and the reagent of the product of reaction. It is not necessary to know the cell constants, since relative values are sufficient to permit locating the equivalence point. The conductance produced by an ion is proportional to its concentration (at constant temperature), but the conductance of a particular solution will in general not vary linearly with added reagent, because of the dilution effect of water being added along with reagent added.

The conductivity of the solution is inversely proportional to the size of the ions. if the size of the ions is increasing then the conductivity of the solution will decrease because the mobility of the ions will decrease by increasing the size of the ions. By increasing the temperature, the mobility of the ions in the solution will increase. So temperature has a direct effect on conductance of solution.
Upon adding a strong base to a mixture of strong acid and weak acids the following reactions occur sequentially

\[
\begin{align*}
[H^+ + Cl^-] & \quad + \quad [Na^+ + OH^-] \quad \rightarrow \quad Na^+ + Cl^- + H_2O \\
CH_3COOH & \quad + \quad [Na^+ + OH^-] \quad \rightarrow \quad CH_3COO^- + Na^+ + H_2O
\end{align*}
\]

According to Kohlrausch law, the electrical conductance of a solution depends upon number/concentration, mobility/speed of ions and temperature. As the titration proceeds, first strong acid reacts or neutralises with base and the conductance of the solution gradually decreases. This continues until the neutralization of strong acid. Further, weak acid reacts with the strong base, conductance increases slowly. After fully neutralization weak acid causes sudden increase in conductance. From the sharp break in the curves, equivalence points can be determined, from which the strength of the acids can be calculated.

Strong base (NaOH) neutralizes the strong acid (HCl) first rather than weak acid (AcOH) indicated by decrease in conductance. This is due to common ion effect. Due to this, dissociation of weak electrolyte is suppressed. Hence, AcOH remains un-neutralized till the complete neutralization of strong electrolyte (HCl). Then start the neutralization of AcOH indicated by increase in conductance values. When the acid mixture is completely neutralized, further addition of base will results the increase in conductance.

**Procedure:** Take 25 mL of 0.1M HCl and 25 mL 0.1M AcOH in a clean 100 mL beaker. Connect the conductivity cell to the conductivity meter. Once the conductivity meter is standardized, add 1mL of 0.5M NaOH from the burette to solution (acid mixture) containing beaker. Stir the solution carefully and note down the corresponding conductance value. Continue the addition of NaOH solution from the burette and record the conductance after every addition and tabulate the data.
Tabular form:

<table>
<thead>
<tr>
<th>S. No</th>
<th>Volume of NaOH (mL)</th>
<th>Conductance (m mho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Model graph:

Plot a graph between conductance values against the volume of the NaOH added. Three straight lines are obtained. The intersection of the first two lines gives the end point of strong acid and the intersection of the second and third lines gives the end point of the weak acid.
Result:
The volume of NaOH (0.5M) required for the strong acid in a given mixture = ……mL

The volume of NaOH (0.5M) required for the weak acid in a given mixture = ……mL

Strength/Concentration of given HCl solution is ………M

Strength/Concentration of given AcOH solution is ………M
2. DETERMINATION OF THE HYDROLYSIS CONSTANT OF ANILINE HYDROCHLORIDE

**Aim:** To determine the hydrolysis constant of aniline hydrochloride by conductometry

**Apparatus:** Beakers, Standard flask, Pipette etc

**Chemicals required:** Aniline hydrochloride (0.1M), aniline

**Principle:** A hydrolysis constant is equilibrium constant for a hydrolysis reaction

When a salt formed from a strong acid and a weak base is dissolved in water forms the cations (Anilinium ions), which are the conjugate acid ions of the weak base, will react with water to form (H\(_3\)O\(^+\)) hydroniuin ions and molecules of the weak base. The anions of the strong acid exhibit little or no tendency to react with the water.

\[
\text{NH}_3\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{PhNH}_2 + \text{H}_3\text{O}^+ + \text{Cl}^-
\]

When anilinium hydrochloride, C\(_6\)H\(_5\)NH\(_3\)Cl is dissolved in water, the chloride ions do not react with the solvent. The anilinium ions take part in the following hydrolysis reaction to form the weak base aniline

\[
\text{NH}_3\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{OH} + \text{HCl} \rightarrow \text{PhNH}_2 + \text{H}_2\text{O}
\]
Aniline hydrochloride undergoes hydrolysis as follows

\[
C_6H_5NH_3Cl + H_2O \rightarrow C_6H_5NH_2 + HCl
\]

\[
\begin{array}{ccc}
1-h & h & h \\
\end{array}
\]

\[
C \times (1-h) \quad C \text{ hCh}
\]

1 mole per liter = (1-h)

C moles per liter = C (1-h)

Where h is the degree of the hydrolysis.

The conductance of the aniline hydrochloride salt solution is due to the ions of aniline hydrochloride salt and HCl formed during hydrolysis.

Let

\[\lambda = \text{Conductance of salt solution}\]

\[\lambda_s = \text{Conductance of aniline hydrochloride salt (presence of aniline)}\]

\[\lambda_{HCl} = \text{Conductance of HCl}\]

Total conductance \[\lambda = (1-h) \lambda_s + h \lambda_{HCl}\]

\[
\begin{align*}
\lambda &= \lambda_s + h \lambda_s + h \lambda_{HCl} \\
\hat{\lambda} - \lambda_s &= h \lambda_{HCl} - h \lambda_s \\
\hat{\lambda} - \lambda_s &= h (\lambda_{HCl} - \lambda_s)
\end{align*}
\]
Degree of hydrolysis, $h = \frac{s - HCl}{HCl - s}$

Hydrolysis constant $k_h$ is given by

$$K_h = \frac{[\text{Aniline}] [\text{HCl}]}{[\text{Aniline hydrochloride}]}$$

$$\frac{h \cdot h}{(1-h)} = \frac{h^2}{(1-h)} \quad \text{for 1 mole}$$

Therefore for ‘C’ moles/lit

$$K_h = \frac{C \cdot h^2}{1-h}$$

$\lambda$ is determined by measuring the conductance of the salt solution.

$\lambda_{HCl}$ has been considered as conductance of HCl at infinite dilution because of the concentration of HCl is very low. $\lambda_s$ is determined by adding few drops of aniline in the salt solution. On addition of aniline; hydrolysis reaction is suppressed due to common ion effect.

**Procedure:**

0.1M aniline hydrochloride solution is prepared by dissolving an accurate amount of salt in distilled water. The conductance of the solution is measured. Few drops of aniline (1mL) are added to the solution and the conductance is measured again. This gives the conductance of un-hydrolysed salt of the dilution of 0.1M. Now, 0.05M, 0.025M, 0.0125M, 0.00625M concentration solutions are prepared from the original 0.1M solution by diluting them with distilled water. The conductance of each solution is measured first without aniline and then by adding few drops of aniline. Tabulate the results as given below

**Model tabular form:**
### Model graph:
Plot a graph between $\frac{h^2}{1-h}$ Vs $\frac{1}{C}$ straight line passing through the origin is obtained. Slope of the line is equal to $K_h$

![Graph Diagram](image)

**Result:** Hydrolysis constant of aniline hydrochloride = ........ mole/lit (From calculations)

From graph, $K_h = ........$ mole/lit
3. DETERMINATION OF SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALT

**Aim:** To determine the solubility product of sparingly soluble salt using conductometer

**Apparatus:** 100ml beaker, conductometer

**Chemicals required:** 0.1M AgNO₃, 0.1M KCl.

**Principle:** The salts which are soluble only to a very little extent are known that is dissolved in a saturated solution may be regarded as present at infinite dilution as sparingly soluble salts. Ex: AgCl, BaSO₄, PbSO₄ etc... As the solubility of sparingly soluble salt is very low, the small n. Thus, its equivalent conductance may be taken as conductance at infinite dilution, \( \lambda_\infty \).

Suppose the solubility of salt is ‘S’ gram equivalents per liter, then the volume which will contain 1 gram equivalents of the salt will be 1000mL. Now the equivalent conductance at infinite dilution is given by:

\[
\lambda_\infty = \lambda_v = \frac{1000 k_v}{S}
\]

\[
S = \frac{1000 k_v}{\lambda_\infty}
\]

The specific conductance \( (k_v) \) of the solution is known by determining the conductance and subtracting it from that of water.

True or observed conductance \( C_T = C_{\text{solution}} - C_{\text{water}} \)

Here, \( k_v = C_T \cdot \text{Cell constant} \).

By determining the solubility of a sparingly soluble salt, one can determine the solubility product of AgCl by substituting it in the equation

\[
K_{sp} = S \cdot S = S^2
\]
**Procedure:** In 100ml beaker, take about 25ml of 0.1M AgNO$_3$ and 25ml of 0.1M KCl. Stir well. Note down the observed conductance.

**Model tabular form:**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Conductance (ms)</th>
<th>Specific conductance ($k_s$)</th>
<th>Solubility (S)</th>
<th>$K_{sp} = \text{Solubility product} \text{ (mol/lit)}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

**RESULT:** The solubility product of AgCl was determined to be:
potentiometry

1. Titration of Fe$^{+2}$ vs Cr$_2$O$_7^{2-}$(Redox titration)

**Aim:** To find out the strength of the given ferrous ammonium sulphate solution by titrating it against potassium dichromate solution potentiometrically.

**Apparatus:** Potentiometer, standard cell, SCE, Pt wire, 100mL beakers, pipette

**Chemicals Required:** 0.1N Ferrous ammonium sulphate (FAS), 0.1N Potassium dichromate (M/60 K$_2$Cr$_2$O$_7$), 6N H$_2$SO$_4$, H$_3$PO$_4$

**Principle:** Potentiometric methods of analysis are based upon measurements of the potential of electrochemical cells under conditions of zero current, where the Nernst equation governs the operation of potentiometry.

Redox reaction involved is given below

$$6\text{Fe}^{2+} \rightarrow 6\text{Fe}^{3+} + 6e^- \quad \text{(Oxidation)} \quad E^0 = 0.77V$$

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad \text{(Reduction)} \quad E^0 = 1.33V$$

**Overall reaction:**

$$6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

Above reaction involves 6e$^-$ transfer between Fe$^{+2}$ and Cr$^{+6}$

The cell can be depicted as follows

Hg (l), Hg$_2$Cl$_2$(S) | KCl || Fe$^{+2}$, Fe$^{+3}$, Pt (or) SCE || Cr$^{+6}$, Cr$^{+3}$, Fe$^{+2}$, Fe$^{+3}$, Pt

$$E_{\text{cell}} = E_{\text{Fe}} - E_{\text{SCE}}$$

$$E_{\text{Fe}} = E_{\text{Fe}}^0 + 0.0591\log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E_{\text{Fe}} = E_{\text{Fe}}^0 + 0.0591\log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} - 0.242$$

As the titration proceeds, i.e. when the K$_2$Cr$_2$O$_7$ is added to ferrous ammonium sulphate, ferric (Fe$^{3+}$) concentration increases and ferrous (Fe$^{+2}$) concentration decreases. Therefore, half-cell potential and the cell potential increases. Near the
end point the rate of change in potential will be maximum as the $[\text{Fe}^{+3}]/[\text{Fe}^{+2}]$ ratio changes significantly. On crossing the equivalence point, EMF changes in small increments and finally it reaches saturation. This is due to, after equivalence point, only $\text{Fe}^{+3}$ ions are present and since no $\text{Fe}^{+2}$ ions are present in solution. After end point the cell potential is governed by other redox couple $[\text{Cr}^{+6}]/[\text{Cr}^{+3}]$.

Actually the electrode potential depends on the concentration of $\text{H}^+$ ions besides the concentration of $\text{Fe}^{+2}$ and $\text{Fe}^{+3}$. Therefore, to avoid the effect of change in the $[\text{H}^+]$ on the electrode potential, this titration is carried out in presence of large amount of $[\text{H}^+]$. Hence the cell potential is depends on concentrations of $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio. Acidic solutions such as $\text{H}_2\text{SO}_4$ and/ or $\text{H}_3\text{PO}_4$ are used to avoid hydrolysis of $\text{Fe}^{+2}$. Phosphoric acid forms complexes with $\text{Fe}^{+3}$, lowering the concentration of simple $\text{Fe}^{+3}$ ions and decreasing the potential of the $\text{Fe}^{+3}/\text{Fe}^{+2}$ couple.

**Procedure:** Take 20mL of 0.1N ferrous ammonium sulphate (FAS) in a 100mL beaker, add 5mL of 6N $\text{H}_2\text{SO}_4$ or $[\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4$ mixture] to the beaker and add sufficient amount of distilled water (25 mL) so that the electrodes are completely dipped in the solution. Combine the Pt electrode (contact electrode) with the calomel electrode through a salt bridge. The two electrodes are connected to the potentiometer. Once the potentiometer is standardized, add 1mL of 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$ from the micro burette to FAS taken in a beaker. Stir the solution carefully and note down the corresponding EMF value. Continue the addition of $\text{K}_2\text{Cr}_2\text{O}_7$ solution from the burette and note the EMF after every addition and tabulate the data.

**Model Tabular Form:**
<table>
<thead>
<tr>
<th>S. No</th>
<th>Volume of $K_2Cr_2O_7$ (mL)</th>
<th>EMF (mv)</th>
<th>$\Delta E$ (mv)</th>
<th>$\Delta V$ (mL)</th>
<th>$\Delta E/\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>2</td>
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<tr>
<td>4</td>
<td>3</td>
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<tr>
<td>5</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Graph:** (1) Plot a graph between EMF (mV) and volume of $K_2Cr_2O_7$ (mL) added. A sigmoid type curve is obtained. From the graph equivalence point can be determined.

(2) Plot a graph between $\Delta E/\Delta V$ and volume of $K_2Cr_2O_7$, a differential graph is obtained. From the graph equivalence point can be determined.

**Result:** The end point for the titration of 20mL FAS against 0.1N $K_2Cr_2O_7$ is …… mL

Strength/Concentration of given FAS solution is ………M
2& 3. Titration of KCl vs AgNO$_3$ (Precipitation Titration)

**Aim:**
To find the strength of the given KCl solution by titrating it against silver nitrate solution. Also evaluate the solubility product of sparingly soluble salt (AgCl) in water, potentiometrically.

**Apparatus:**
Potentiometer, calomel electrode, silver electrode, salt bridge, beakers, pipette

**Chemicals Required:**
0.1M AgNO$_3$, 0.1M KCl, double distilled water, saturated KCl etc.

**Principle:**
Potentiometric methods of analysis are based upon measurements of the potential of electrochemical cells under conditions of zero current, where the Nernst equation governs the operation of potentiometry. To measure the potential changes, the indicator electrode is coupled with a reference electrode using a salt bridge.

Precipitation titration is based on a reaction that yields ionic compounds of limited solubility. The number of precipitating agents that can be used is limited due to the slow rate of formation of precipitates. The widely used precipitation reagent is silver nitrate, and precipitation titration based on silver nitrate is known as argentometric methods.

The precipitation reaction between KCl and AgNO$_3$ is shown below

$$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl(S)} K_{sp} = 1.82 \times 10^{-10} \text{M}^2$$

The cell can be depicted for the precipitation titration as follows

**Cell notation:**

\[
\text{Hg (l), Hg}_2\text{Cl}_2(S) \mid \text{KCl} \parallel \text{Ag}^+, \text{Ag} \\
E_{\text{Cell}} = E_{\text{Ag}} - E_{\text{SCE}} \\
E_{\text{Ag}} = E^O_{\text{Ag}} - (2.303RT/F) \log (1/\text{Ag}^+) \\
E_{\text{Cell}} = E^O_{\text{Ag}} - (2.303RT/F) \log (1/\text{Ag}^+) - 0.242 \\
E_{\text{Cell}} = E^O_{\text{Ag}} + (2.303RT/F) \log [\text{Ag}^+] - 0.242 \\
E_{\text{Cell}} = 0.80 + 0.0591 \log (\text{Ag}^+) - 0.242
\]
\[ E_{\text{Cell}} = 0.558 + 0.0591 \log (\text{Ag}^+) \]

\[ E_{\text{Cell}} \text{ is directly proportional to } [\text{Ag}^+] \]

In this precipitation titration, silver electrode is used as an indicator/working electrode. As the titration proceed, i.e. when the AgNO\(_3\) is added to KCl solution (taken in a beaker), Cl\(^-\) concentration decreases and Ag\(^+\) concentration increases. Therefore, the halfcell potential as well as the cell potential increases. Near the end point the rate of change in potential will be maximum due to completion of precipitation. On crossing the equivalence point, EMF changes in small increments and finally it reaches saturation.

**Determination of solubility product of AgCl:**

From EMF measurements,

\[ E_{\text{Cell}} = 0.558 + 0.0591 \log (\text{Ag}^+) \]

To the determination of [Ag\(^+\)], substitute the \(E_{\text{cell}}\) value corresponding to half of the volume required for the end point of the titration in the following equation

\[ [\text{Ag}^+] = 10^{\left(\frac{E_{\text{cell}}-0.558}{0.0591}\right)} \]

**Solubility product, \(K_{sp} = [\text{Ag}^+] [\text{Cl}^-]\)**

**Procedure:** Take 10mL of 0.1M KCl solution in a 100mL beaker and add sufficient water so that the Ag electrode is completely dipped (40 mL double distilled water) in solution. Combine the Ag electrode with the calomel electrode through a salt bridge. The two electrodes are connected to the potentiometer. Once the potentiometer is standardized, add 1mL of 0.1M AgNO\(_3\) from the micro burette to KCl solution taken in beaker. Stir the contents well. Note the corresponding EMF. Now go on adding AgNO\(_3\) solution from the burette and note the EMF after every addition. Tabulate the readings.

**Model Tabular Form:**
Graph: (1) Plot a graph between EMF and volume of AgNO₃. This gives an equivalence point for the titration (sigmoid curve)

(2) Plot a graph between $\Delta E/\Delta V$ and volume of AgNO₃. A differential graph is obtained.

Model Graphs:
**Result:**

The end point for the titration of 10mL KCl solution against 0.1N AgNO$_3$ is ……. mL

Strength/Concentration of given KCl solution is ………M

Solubility product, (K$_{sp}$) = ……………….mole$^2$/lit$^2$

**Note:**

As the titration proceed, i.e. when the KCl is added to AgNO$_3$ solution (taken in a beaker), Cl$^-$ concentration increases and Ag$^+$ concentration decreases. Therefore, the half cell potential as well as the cell potential decreases. Near the end point the rate of change in potential will be maximum due to completion of precipitation. On crossing the equivalence point, EMF decreases gradually and finally it reaches saturation.

**Model graph:**

![Model graph](image)
POLARIMETRY

DETERMINATION OF SPECIFIC ROTATION OF GLUCOSE

Aim: Determination of specific rotation of glucose at various concentrations using Polarimeter

Apparatus: Polarimeter, sodium vapour lamp, standard flask, pipette, beaker, funnel

Chemicals: Glucose solution, distilled water etc

Principle: Specific rotation is the optical rotation made by an optically active compound solution when the concentration of the solution is 1g/ml and the length of tube is 1dm. In the polarimeter, the glucose solution is placed between the polarizer and the analyzer set in the complete extinction position, some light starts coming through the analyzer and the optical view appears somewhat less bright or shaded. This is due to the fact that the rays emerging from the solution vibrate at an angle to the initial plane of polarization of light. This rotation of polarised light is due to the absence of symmetry in the molecules. The analyzer has to be rotated through an angle α to set it again in the complete extinction position. If the rotation is done in clockwise direction, the substance is dextrorotatory. If the analyzer is rotated in anti-clockwise direction, the substance is laevorotatory.

Calibration of the polarimeter:

Set up a sodium vapour lamp at a distance equal to the focal length of the lens(about 9cm) from the end point of the polarimeter. Adjust the height of the lamp and the optical axis of the instrument for maximum illumination of the polarizer. Take a properly cleaned polarimeter tube, fill the tube with distill water. Avoid entry of air bubbles into the tube. There should be no liquid drops on the outside of the glass plate windows. Place the tube between polarizer and analyzer and focus it on the light shaded boundary in the field of view. Determine the zero point of the two halves of the field of view are equally dark. The reading on the scale is read through the scale eye piece. If this reading is not exactly zero, an adjustment may be made in the instrument if provided in the instrument or this reading is recorded and used for correcting the subsequent readings.
**Calculations:**

The value of specific rotation is calibrated using the formulae

\[ \alpha = \frac{100 \times \theta}{1 \times c} \]

Where \( l \rightarrow \) length of the polarimeter tube = 2dm

\( c \rightarrow \) concentration of the solution

\( \theta \rightarrow \) angle of rotation (corrected value)

**Procedure:** When the calibration has been done, the tube can be raised with and filled with solution whose optical activity is to be measured and the measurements are carried out in the same manner as in calibration step. Reading is repeated 5 times and the average value for optical rotation is used, glucose of 20%, 10%, 5%, 2.5% are used and the optical rotation is obtained for each of them.

**MODEL TABULAR FORM:**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of glucose solution (%)</th>
<th>Angle of rotation (θ)</th>
<th>Specific rotation (degree lit mol(^{-1})dm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
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<tr>
<td>3</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Model graph:**

A graph is drawn taking angle of rotation on Y-axis and concentration of solution in % on X-axis which gives a straight line passing through the origin. The value of specific rotation is calculated from the slope value.

![Graph showing angle of rotation and concentration](image)

Slope=$\alpha \times l / 100$

**Result:**

The specific rotation of glucose (From calculations) =

The specific rotation of glucose (From graph) =

Repeat the similar experimental procedure for Sucrose and Fructose
INVERSION OF SUCROSE

**Aim:** To determine inversion of sucrose by following the kinetics of acid catalyzed hydrolysis of sucrose under pseudo conditions using polarimeter.

**Apparatus:** Polarimeter, sodium vapour lamp, polarimeter tube, graduated pipette.

**CHEMICALS:** 20% sucrose, distilled water, 2N and 4N HCl

**Principle:**

Inversion of cane sugar in presence of acid may be represented as

\[ C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 \]

Dextro Dextro laevo

The reaction is also an example of pseudo uni molecular reaction. The rate of reaction is determined by concentration of sucrose where the concentration of acid is kept constant. It is represented by

\[ \frac{dx}{dt} \propto [\text{sucrose}] \]

The progress of reaction can be followed by noting the optical activity of solution with help of polarimeter. Cane sugar and glucose are dextro rotator while fructose is strongly leavo rotator at equimolar concentrations. Hence as the reaction proceeds optical rotation of solution gradually decreases from positive to zero and ultimately becomes negative due to increase in formation of products in solution. Hence it is named as inversion of cane sugar.

The reaction is of 1st order with respect to Sucrose, since the concentration of water is taken in large excess and hence the change in water concentration is very less or virtually constant during the course of the reaction. Hence the reaction is referred as Pseudo first order reaction.

Rate constant,
**Procedure:** Take 30ml of 20% solution into a clean beaker. Set up polarimeter, now we add 30ml of 2N HCl to the sugar solution and start the stop clock. Immediately transfer the solution into the polarimeter tube and note the angle of rotation for every 5 minutes. After 1 hour take out remaining mixture and heat at 60°C, note the angle of rotation of this mixture as infinite reading ($r_\infty$). The rate constant can be calculated by using formula

$$k = \frac{2.303}{t} \log \left[ \frac{r_0 - r_\infty}{r_t - r_\infty} \right] \text{ min}^{-1}$$

**Model tabular form:** For 2N HCl

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$r_t$</th>
<th>$r_t - r_\infty$</th>
<th>$\log \left[ \frac{r_0 - r_\infty}{r_t - r_\infty} \right]$</th>
<th>$k = \frac{2.303}{t} \log \left[ \frac{r_0 - r_\infty}{r_t - r_\infty} \right] \text{ min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$r_0 = r_0 - r_\infty$ =</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$r_t - r_\infty = r_0 - r_\infty$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
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</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
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<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>$r_\infty = r_0 - r_\infty$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Repeat the same procedure for 4N HCl.

**Model Graphs:** Plot a graph between \( \log \left( \frac{r_0 - r_\infty}{r_t - r_\infty} \right) \) and time, straight line passing through origin is obtained. From the slope rate constant \( (k) \) can be calculated. Plot another graph between

\[ \log (r_t - r_\infty) \] and time, a straight line with negative slope is obtained.

---

**Result:**

**For 2N HCl**

Rate constant from the experiment data = ……………………. min\(^{-1}\)

Rate constant from the graph - 1 = …………………………. min\(^{-1}\)

Rate constant from the graph - 2 = ……………………………min\(^{-1}\)

**For 4N HCl**

Rate constant from the experiment data = ………………………….. min\(^{-1}\)

Rate constant from the graph - 1 = …………………………….. min\(^{-1}\)

Rate constant from the graph - 2 = …………………………….min\(^{-1}\)

Ratio of rate constants \( (k_{2N} : k_{4N}) \) = ……………………..
COLORIMETRY

VERIFICATION OF BEER’S LAW USING KMnO₄ SOLUTION

Aim: To determine the concentration of given KMnO₄ solution by verifying the Beer’s law using colorimeter.

Apparatus: Colorimeter, graduated pipette, standard flask, test tubes, cuvettes etc.

Chemicals required: 5x10⁻⁴ M KMnO₄ solution, distilled water

Principle: Beer’s law is applicable to only to dilute solutions. It states that when a monochromatic light is passed through a solution intensity of light decreases with thickness and this decrease in intensity is directly proportional to the intensity of incident light and the concentration of the solution.

\[ I = I_0 e^{-\varepsilon c x} \]

Where \( I \) = Intensity of the transmitted light; \( I_0 \) = Intensity of the incident light

\( C \) = Concentration of the solution; \( x \) = Path length of the cuvette

\( \varepsilon \) = Molar extinction coefficient

\[ \frac{I}{I_0} = e^{-\varepsilon c x}, \quad \ln\left(\frac{I}{I_0}\right) = -\varepsilon c x \]

The value of \( \varepsilon \) (epsilon) depends on the nature of the absorbing solute but independent of the concentration of the solution. Decrease in the intensity of the transmitted light is due to the absorption of light, which may lead to photochemical reactivity.

In colorimetric studies transmittance is defined as the fraction of light passes through the sample

\% Transmittance \((T) = \left(\frac{I}{I_0}\right) \times 100\)

A more useful and convenient quantity in performing analysis is the absorbance or negative log of transmittance.

Absorbance or Optical density\( = A = \log \left(\frac{1}{T}\right) = -\log \left(T\right)\)
A linear relation exists between absorbance (O. D) and concentration of the sample is known as Beer’s law.

Absorbance or Optical density = A = \log (I_0/I) = \varepsilon cx

Before verification of Beer’s law, it is necessary to select a suitable wavelength and determines whether Beer’s law is valid at the wavelength selected. The most suitable wavelength is that at which maximum absorbance is observed, called \( \lambda_{\text{max}} \). The \( \lambda_{\text{max}} \) will always be at the same wavelength for a given solution under any condition.

**Procedure:** Colorimeter is switched on, wait for 10-15min so that the instrument acquires temperature stability. The intensity of the light from the lamp depends on the environmental temperature. Now transmittance is adjusted to 100\% or O.D is adjusted to zero with distilled water (Since water is the solvent used in the preparation of KMnO\(_4\) solution), which is taken in a cuvette. By using various filters the \( \lambda_{\text{max}} \) value of the KMnO\(_4\) solution (Purple or violet colour solution) can be determined. Different concentrations of KMnO\(_4\) solutions are prepared by mixing 10,9,8,7,6,5,4,3,2,1 ml KMnO\(_4\) solutions from the stock with 0,1,2,3,4,5,6,7,8,9 ml of distilled water respectively. The O.D value is measured for each set at the \( \lambda_{\text{max}} \) which is in the range of 520-540nm (green colour filter).

**Model tabular form: a) Filter selection**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Wavelength(nm)</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
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<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
b) Beer’s law verification

<table>
<thead>
<tr>
<th>S.No</th>
<th>Volume of KMnO₄ (ml)</th>
<th>Volume of water (ml)</th>
<th>Concentration (mol/lit)</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>1</td>
<td>4.5 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>2</td>
<td>4.0 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>3</td>
<td>3.5 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4</td>
<td>3.0 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>2.5 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>6</td>
<td>2.0 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>7</td>
<td>1.5 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>8</td>
<td>1.0 \times 10^{-4}M</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>9</td>
<td>0.5 \times 10^{-4}M</td>
<td></td>
</tr>
</tbody>
</table>

**Model graph**: A graph is plotted between optical density and concentration of KMnO₄. A straight line passing through the origin is obtained. Molar extinction coefficient can be determined from the slope of the line.

Calibration curve

![O.D and Concentration graph](attachment:image.png)

![Transmittance and Concentration graph](attachment:image.png)
**Result:** A straight line passing through origin is obtained in the graph. Hence, Beer’s law is verified.

The molar extinction co-efficient = .......... Lit mol$^{-1}$ cm$^{-1}$
**VERIFICATION OF BEER’S LAW USING CuSO₄ SOLUTION**

**Aim:** To determine the concentration of given CuSO₄ solution by verifying the Beer’s law using colorimeter.

**Apparatus:** Colorimeter, graduated pipette, standard flask, test tubes, cuvettes etc.

**Chemicals required:** 0.2M CuSO₄ solution, distilled water

**Principle:** Beer’s law is applicable to only to dilute solutions. It states that when a monochromatic light is passed through a solution intensity of light decreases with thickness and this decrease in intensity is directly proportional to the intensity of incident light and the concentration of the solution.

\[ I = I_0 e^{-\varepsilon c x} \]

Where \( I = \) Intensity of the transmitted light; \( I_0 = \) Intensity of the incident light

\( C = \) Concentration of the solution; \( x = \) Path length of the cuvette

\( \varepsilon = \) Molar extinction coefficient

\[ \frac{I}{I_0} = e^{-\varepsilon cx} , \quad \ln(\frac{I}{I_0}) = -\varepsilon cx \]

The value of \( \varepsilon \) (epsilon) depends on the nature of the absorbing solute but independent of the concentration of the solution. Decrease in the intensity of the transmitted light is due to the absorption of light, which may lead to photochemical reactivity.

In colorimetric studies transmittance is defined as the fraction of light passes through the sample

\[ \% \ Transmittance \ (T) = \left( \frac{I}{I_0} \right) \times 100 \]

A more useful and convenient quantity in performing analysis is the absorbance or negative log of transmittance.

**Absorbance or Optical density = \( A = \log \left( \frac{1}{T} \right) = - \log \ (T) \)**

A linear relation exists between absorbance (O. D) and concentration of the sample is known as Beer’s law.
Absorbance or Optical density= \( A = \log \left( \frac{I_0}{I} \right) = \varepsilon cx \)

Before verification of Beer’s law, it is necessary to select a suitable wavelength and determines whether Beer’s law is valid at the wavelength selected. The most suitable wavelength is that at which maximum absorbance is observed, called \( \lambda_{\text{max}} \). The \( \lambda_{\text{max}} \) will always be at the same wavelength for a given solution under any condition.

**Procedure:** Colorimeter is switched on, wait for 10-15min so that the instrument acquires temperature stability. The intensity of the light from the lamp depends on the environmental temperature. Now transmittance is adjusted to 100% or O.D is adjusted to zero with distilled water (Since water is the solvent used in the preparation of CuSO\(_4\) solution), which is taken in a cuvette. By using various filters the \( \lambda_{\text{max}} \) value of the CuSO\(_4\) solution (Bluish green colour solution) can be determined. Different concentrations of CuSO\(_4\) solutions are prepared by mixing 10,9,8,7,6,5,4,3,2,1 ml CuSO\(_4\) solutions from the stock with 0,1,2,3,4,5,6,7,8,9 ml of distilled water respectively. The O.D value is measured for each set at the \( \lambda_{\text{max}} \) which is in the range of 650-700nm (Red colour filter).

**Model tabular form: a) Filter selection**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Wavelength(nm)</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
b) Beer’s law verification

<table>
<thead>
<tr>
<th>S. No</th>
<th>Volume of CuSO₄ (ml)</th>
<th>Volume of water (ml)</th>
<th>Concentration (mol/lit)</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>9</td>
<td>1</td>
<td>0.18</td>
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</tr>
<tr>
<td>2.</td>
<td>8</td>
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<td>0.16</td>
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<td>3.</td>
<td>7</td>
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<td>7</td>
<td>0.06</td>
<td></td>
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<td>1</td>
<td>9</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

**Model graph:** A graph is plotted between optical density and concentration of CuSO₄. A straight line passing through the origin is obtained. Slope of the line is equal to Molar extinction co-efficient.
**Result:** A straight line passing through origin is obtained in the graph. Hence, Beer’s law is verified.

The molar extinction co-efficient = ........... Lit mol\(^{-1}\) cm\(^{-1}\)
**P**H**M**ETRY

**PREPARATION OF PHOSPHATE BUFFER:**

**Aim:** To prepare phosphate buffers and verify their working in various compositions in the mixture.

**Chemicals:** KH$_2$PO$_4$, Na$_2$HPO$_4$, buffer tablets for pH 4, 7 & 9

**Procedure:**
1. Calibrate the pH meter using standard buffer solution of pH = 4/9/7.
2. Prepare the phosphate solutions viz., M/15 KH$_2$PO$_4$ & M/15 Na$_2$HPO$_4$
3. Make a mixture of these two solutions in the following compositions to obtain phosphate buffer solution and record the pH by dipping a combined electrode (glass electrode) duly connected to the pH meter.

<table>
<thead>
<tr>
<th>Vol. of KH$_2$PO$_4$</th>
<th>1.0ml</th>
<th>2.0ml</th>
<th>3.0ml</th>
<th>4.0ml</th>
<th>5.0ml</th>
<th>6.0ml</th>
<th>7.0ml</th>
<th>8.0ml</th>
<th>9.0ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. of Na$_2$HPO$_4$</td>
<td>9.0ml</td>
<td>8.0ml</td>
<td>7.0ml</td>
<td>6.0ml</td>
<td>5.0ml</td>
<td>4.0ml</td>
<td>3.0ml</td>
<td>2.0ml</td>
<td>1.0ml</td>
</tr>
</tbody>
</table>
Observations & tabulation:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Volume of KH$_2$PO$_4$ (ml)</th>
<th>Volume of Na$_2$HPO$_4$ (ml)</th>
<th>Conc. of KH$_2$PO$_4$ (M)</th>
<th>Conc. of Na$_2$HPO$_4$ (M)</th>
<th>pH of the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>9</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<tr>
<td>9</td>
<td>9</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

GRAPH:

\[ \text{pH} \]

Intercept = pK$_a$

\[ \log[\text{NaHPO}_4]/[\text{K}_2\text{HPO}_4] \]

Calculations:

The working of the prepared buffer solution i.e., pH is verified using Henderson’s equation: \( \text{pH} = \text{pK}_a + \log[\text{NaHPO}_4]/[\text{K}_2\text{HPO}_4] \)

Result: The phosphate buffer is prepared and verified for its working using Henderson’s equation.