UG LABORATORY MANUAL

Department of Chemistry, Jhargram Raj College

UNDERGRADUATE LABORATORY MANUAL

Department of Chemistry (UG & PG)
Jhargram Raj College, Jhargram

[For Honours/MDS curriculum under the CCFUP/NEP 2020 (Semesters-I and II) and CBCS curriculum (Semester-III to Semester-VI) of Vidyasagar University]

PART – I: EXPERIMENTS IN PHYSICAL CHEMISTRY

CONTENTS

SEMESTER – I
(UNDER THE CCFUP, NEP 2020)
[FOR HONOURS MINOR, PAPER: CEMMI01P]

Experiment 1: Determination of the relative surface tension ratio and the relative surface tension of liquids or dilute solutions using a stalagmometer.

Theory: The surface tension of a pure liquid/solution can be measured either by using the drop-weight or the capillary rise method. Here we implement the drop-weight (equivalent to the drop-counting) method to determine the surface tension of the supplied solution or liquid. The principle of the drop-weight method is based on the fact that when a liquid is allowed to flow through a capillary tube (thus ensuring almost streamline flow) and fall in drops from its end, the drop first remains sticking at the end of the capillary tube, but it falls down when its weight becomes just equal to the force of surface tension, acting on it.

The weight w of a drop of liquid of density ρ and volume v is given by

$$w = v\rho g.$$

If the radius of the drop be r, and if γ be the surface tension acting on it, then the force due to surface tension is $2\pi r\gamma$, where $2\pi r$ is the circumference of the liquid drop. If there are n drops in a finite volume V, then the volume of a single drop, $v = V/n$. Therefore, under the condition of equilibrium

$$2\pi r\gamma = \frac{V\rho g}{n}$$

If two different liquids of densities ρ_A and ρ_B and surface tensions γ_A and $\gamma_B$are allowed to flow in equal volumes V through the same stalagmometer, and if n_A and n_B be the number of drops that make up for the volume V, then we must have

$$2\pi r\gamma_A = \frac{V\rho_A g}{n_A} \quad \text{and} \quad 2\pi r\gamma_B = \frac{V\rho_B g}{n_B},$$

so that

$$\frac{\gamma_A}{\gamma_B} = \frac{\rho_A}{\rho_B} \cdot \frac{n_B}{n_A}$$

Thus, if the surface tension and the density of one of the liquids be known, n_A and n_B can be experimentally found out, the density be determined and the unknown surface tension can be evaluated. Generally, water is used as the reference liquid and the last equation modifies to

$$\frac{\gamma_X}{\gamma_{H_2O}} = \frac{\rho_X}{\rho_{H_2O}} \cdot \frac{n_{H_2O}}{n_X},$$

where X stands for the unknown liquid. The surface tension obtained in accordance of the aforesaid method is the *relative* surface tension, and not the absolute surface tension, since it is determined relative to the surface tension of the reference liquid.

Procedure: *(Please do not report in your laboratory notebook)*

1. Rinse the stalagmometer with distilled water and drain out the water thoroughly.
2. Clamp the stalagmometer vertically. Suck distilled water through the stalagmometer and release it and start to count the number of drops as the meniscus touches the upper mark of the bulb of the stalagmometer. Keep counting the drops till the meniscus touches the lower mark of the bulb. Repeat the process twice, and calculate the average time of flow.
3. Remove the water completely from the stalagmometer and rinse it with a small amount of the supplied liquid SA, discard the liquid after rinsing. Repeat step 2 with SA and note down the drop count.
4. Remove the solution SA completely from the viscometer and rinse it with a small amount of water followed by a small amount of the supplied liquid SB; discard the liquid after rinsing. Repeat step 2 with SB and note down the drop count.

5. Using a clean and dry specific gravity bottle determine the specific gravities of the supplied solutions SA and SB.
6. Calculate the relative surface tension ratios and the relative surface tensions of SA and SB.

Results and Calculations:

1. Experimental temperature: …… °C
   Given: Density of water at **……** °C = **……** g/ml.
   Surface tension of water at **……** °C = **……** dynes/cm.
2. Determination of the specific gravities:

Sl. No.	Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
1	Empty		×	×	×
2	Water				
3	Solution-A (SA)				
4	Solution-B (SB)				

3. Determination of the relative surface tension ratios (γ_X/γ_{H_2O}):

Sl. No.	Substance	No. of Obs.	Drop Count	Mean Drop Count	Relative surface tension ratio (γ_X/γ_{H_2O})
1.	Water	1.			
		2.			
		3.			
2.	Solution-A (VA)	1.			
		2.			
		3.			
3.	Solution-B (VB)	1.			
		2.			
		3.			

Conclusion: The relative surface tension ratios of the liquids SA and SB are …… and ……, and the relative surface tensions are …… dynes/cm and …… dynes/cm, respectively at …… °C.

Experiment 2: Determination of the relative surface tension ratios and the relative surface tensions of liquids or dilute solutions using a stalagmometer and hence to determine the unknown concentration of a solution.

Theory: The surface tension of a pure liquid/solution can be measured either by using the drop-weight or the capillary rise method. Here we implement the drop-weight (equivalent to the drop-counting) method to determine the surface tension of the supplied solution or liquid. The principle of the drop-weight method is based on the fact that when a liquid is allowed to flow through a capillary tube (thus ensuring almost streamline flow) and fall in drops from its end, the drop first remains sticking at the end of the capillary tube, but it falls down when its weight becomes just equal to the force of surface tension, acting on it.

The weight w of a drop of liquid of density ρ and volume v is given by

$$w = v\rho g.$$

If the radius of the drop be r, and if γ be the surface tension acting on it, then the force due to surface tension is $2\pi r\gamma$, where $2\pi r$ is the circumference of the liquid drop. If there are n drops in a finite volume V, then the volume of a single drop, $v = V/n$. Therefore, under the condition of equilibrium

$$2\pi r\gamma = \frac{V\rho g}{n}$$

If two different liquids of densities ρ_A and ρ_B and surface tensions γ_A and $\gamma_B$are allowed to flow in equal volumes V through the same stalagmometer, and if n_A and n_B be the number of drops that make up for the volume V, then we must have

$$2\pi r\gamma_A = \frac{V\rho_A g}{n_A} \quad \text{and} \quad 2\pi r\gamma_B = \frac{V\rho_B g}{n_B},$$

so that

$$\frac{\gamma_A}{\gamma_B} = \frac{\rho_A}{\rho_B} \cdot \frac{n_B}{n_A}$$

Thus, if the surface tension and the density of one of the liquids be known, n_A and n_B can be experimentally found out, the density be determined and the unknown surface tension can be evaluated. Generally, water is used as the reference liquid and the last equation modifies to

$$\frac{\gamma_X}{\gamma_{H_2O}} = \frac{\rho_X}{\rho_{H_2O}} \cdot \frac{n_{H_2O}}{n_X},$$

where X stands for the unknown liquid. The surface tension obtained in accordance of the aforesaid method is the *relative* surface tension, and not the absolute surface tension, since it is determined relative to the surface tension of the reference liquid.

Procedure: *(Please do not report in your laboratory notebook)*

1. Rinse the stalagmometer with distilled water and drain out the water thoroughly.
2. Clamp the stalagmometer vertically. Suck distilled water through the stalagmometer and release it and start to count the number of drops as the meniscus touches the upper mark of the bulb of the stalagmometer. Keep counting the drops till the meniscus touches the lower mark of the bulb. Repeat the process twice, and calculate the average time of flow.
3. Remove the water completely from the stalagmometer and rinse it with a small amount of the supplied liquid 3%, discard the liquid after rinsing. Repeat step 2 with the 3% solution and note down the drop count.
4. Remove the 3% solution completely from the stalagmometer and rinse it with a small amount of water followed by a small amount of the supplied 6% solution; discard the liquid after rinsing. Repeat step 2 with 6% and note down the drop count.
5. Repeat steps 2, 3, and 4 with the 9% and 12% solutions, and the solution marked X.
6. Using a clean and dry specific gravity bottle determine the specific gravities of the supplied solutions (3%, 6%, 9%, 12% and X).
7. Calculate the relative surface tension ratios and the relative surface tensions of the supplied solutions (3%, 6%, 9%, 12% and X).
8. Plot the concentrations in % (along X axis) and the surface tension values (along Y axis) and draw a free-hand curve. From the value of the surface tension of the solution marked X, determine its concentration.

Results and Calculations:

1. Experimental temperature: …… °C
   Given: Density of water at **……** °C = **……** g/ml.
   Surface tension of water at **……** °C = **……** dynes/cm.
2. Determination of the specific gravities:

Sl. No.	Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
1	Empty		×	×	×
2	Water				
3	3% solution				

4	6% solution				
5	9% solution				
6	12% solution				
7	X% solution				

3. Determination of the relative surface tension ratios (γ_X/γ_{H_2O}):

Sl. No.	Substance	No. of Obs.	Drop Count	Mean Drop Count	Relative surface tension ratio (γ_X/γ_{H_2O})
1.	Water	1.			
		2.			
		3.			
2.	3%	1.			
		2.			
		3.			
3.	6%	1.			
		2.			
		3.			
4.	9%	1.			
		2.			
		3.			
5.	12%	1.			
		2.			
		3.			
6.	X%	1.			
		2.			
		3.			

Conclusion: From the graph, the concentration of the solution with unknown concentration has been determined to be …… %, respectively at …… °C.

Experiment 3: Determination of the relative viscosity ratio and the relative viscosity coefficients of liquids or dilute solutions using an Ostwald's viscometer.

Theory: The concept of viscosity is usually met in problems of fluid flow, treated by hydrodynamics, as a measure of the fractional resistance that a fluid in motion offers to an applied shearing force. If a fluid is flowing past a stationary plane surface, the layer of fluid adjacent to the plane boundary is stagnant; successive layers have increasingly higher velocities. The frictional force, F, resisting the relative motion of any two adjacent layers, is proportional to the area of interface, S between them and to the velocity gradient, dv/dr between them. This is known as the Newton's law of viscous flow, and is applicable to nonconservative/dissipative systems only. Thus,

$$F \propto S\frac{dv}{dr} \Rightarrow F = \eta S\frac{dv}{dr} \quad (1)$$

The proportionality constant η is known as the **coefficient of viscosity**, and is the quantity of interest. Thus η may be defined as the force per unit area required to move a layer of fluid with a velocity difference of 1 cm per second past another parallel layer 1 cm away. It is evident that the dimensions of η is $\text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$. The SI unit of η is $\text{kg} \cdot \text{m}^{-1} \cdot \text{sec}^{-1}$, and the CGS unit is $\text{gm} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$ or poise (denoted by P), and is equal to one-tenth the SI unit.

The theory of the process was first worked out by J. L. Poiseuille in 1844. Consider a fluid flowing through a tube of circular cross-section with radius R and length L. The fluid layer in the closest proximity of the walls is assumed to be stagnant, and the rate of flow increases to a maximum at the

centre of the tube. Let v be the linear velocity at any distance r from the axis of the tube. A cylinder of fluid of radius r experiences a viscous drag given by Eq.(1) as

$$F_r = -\eta \frac{dv}{dr} \cdot 2\pi rL \tag{2}$$

For a steady flow, this force must be exactly balanced by the force driving the fluid in this cylinder through the tube. Since the pressure is the force per unit area, the driving force is

$$F_d = \pi r^2 (P_1 - P_2) \tag{3}$$

where P_1 and P_2 are fore and back pressures, respectively. Therefore, for steady flow, $F_r = F_d$, that is

$$-\eta \frac{dv}{dr} \cdot 2\pi rL = \pi r^2 (P_1 - P_2)$$

so that,

$$dv = -\frac{r}{2\eta L}(P_1 - P_2)dr \tag{4}$$

On integration of Eq.(4) we get

$$v = -\frac{(P_1 - P_2)r^2}{4\eta L} + \text{constant of integration} \tag{5}$$

According our hypothesis, $v = 0$, when $r = R$; this boundary condition determines the integration constant, so that

$$v = \frac{(P_1 - P_2)}{4\eta L}(R^2 - r^2) \tag{6}$$

The total volume of fluid flowing through the tube per second dV/dt is calculated by integrating the fluid velocity v over each element of cross-sectional area $2\pi rdr$. Thus,

$$\frac{dV}{dt} = \int_0^R 2\pi rv dr = \frac{\pi(P_1 - P_2)R^4}{8\eta L} \tag{7}$$

This is Poiseuille's equation which applies to incompressible fluids undergoing laminar flow. Poiseuille's equation may be satisfactorily applied to liquids but not to gases, as volume is a strong function of pressure for gases.

Under a constant pressure head $P = P_1 - P_2$, V volume of a liquid is allowed to flow through a fine capillary tube of known radius R. The length L and the time t for the flow are noted. The equation would thus be

$$\eta = \frac{\pi P R^4 t}{8LV} \tag{8}$$

Using the Ostwald viscometer one can measure the relative viscosity of a liquid, relative to the viscosity (known) of another liquid, referred to as the reference liquid. Therefore,

$$\frac{\eta_X}{\eta_{\mathrm{H_2O}}} = \frac{\pi P_X R^4 t_X / 8LV}{\pi P_{\mathrm{H_2O}} R^4 t_{\mathrm{H_2O}} / 8LV} = \frac{P_X t_X}{P_{\mathrm{H_2O}} t_{\mathrm{H_2O}}} = \frac{hg\rho_X t_x}{hg\rho_{\mathrm{H_2O}} t_{\mathrm{H_2O}}}$$

Upon cancellation, we have

$$\frac{\eta_X}{\eta_{\mathrm{H_2O}}} = \frac{\rho_X t_x}{\rho_{\mathrm{H_2O}} t_{\mathrm{H_2O}}} \tag{9}$$

If $\eta_{\mathrm{H_2O}}$ is known, a measurement of the densities and times of flow of the two would yield η_X, the coefficient viscosity of the unknown liquid.

Procedure: *(Please do not report in your laboratory notebook)*

1. Rinse the Ostwald viscometer with distilled water and drain out the water thoroughly.
2. Add 10 ml of distilled water using a 10 ml pipette into the wider limb of the viscometer and clamp it vertically. Suck the water through the narrower limb of the viscometer and release it and start the stop-watch as the meniscus touches the upper mark of the bulb. Allow the water to flow and stop the stop-watch as the meniscus touches the lower mark of the bulb. Repeat the process twice, and calculate the average time of flow.

3. Remove the water completely from the viscometer and rinse it with a small amount of the supplied liquid VA, discard the liquid after rinsing. Repeat step 2 with VA and note down the time of flow.
4. Remove the solution VA completely from the viscometer and rinse it with a small amount of water followed by a small amount of the supplied liquid VB; discard the liquid after rinsing. Repeat step 2 with VB and note down the time of flow.
5. Using a clean and dry specific gravity bottle determine the specific gravities of the supplied solutions VA and VB.
6. Calculate the relative viscosity ratios and the relative viscosity coefficients of VA and VB.

Results and Calculations:

1. Experimental temperature: …… °C
   Given: Density of water at **……** °C = **……** g/ml.
   Coefficient of viscosity of water at **……** °C = **……** poise.
2. Determination of the specific gravities:

Sl. No.	Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
1	Empty		×	×	×
2	Water				
3	Solution-A (VA)				
4	Solution-B (VB)				

3. Determination of the relative viscosity ratios (η_X/η_{H_2O}):

Sl. No.	Substance	No. of Obs.	Time of flow (s)	Mean time of flow (s)	Relative viscosity ratio (η_X/η_{H_2O})
1.	Water	1.			
		2.			
		3.			
2.	Solution-A (VA)	1.			
		2.			
		3.			
3.	Solution-B (VB)	1.			
		2.			
		3.			

Conclusion: The relative viscosity ratios of the liquids VA and VB are …… and ……, and the relative viscosity coefficients are …… poise and …… poise, respectively at …… °C.

Experiment 4: Determination of the relative viscosity coefficient ratios and the relative viscosity coefficients of liquids or dilute solutions using a Ostwald's viscometer and hence to determine the unknown concentration of a solution.

Theory: The concept of viscosity is usually met in problems of fluid flow, treated by hydrodynamics, as a measure of the fractional resistance that a fluid in motion offers to an applied shearing force. If a fluid is flowing past a stationary plane surface, the layer of fluid adjacent to the plane boundary is stagnant; successive layers have increasingly higher velocities. The frictional force, F, resisting the relative motion of any two adjacent layers, is proportional to the area of interface, S between them and to the velocity gradient, dv/dr between them. This is known as the Newton's law of viscous flow, and is applicable to nonconservative/dissipative systems only. Thus,

$$F \propto S\frac{dv}{dr} \Rightarrow F = \eta S\frac{dv}{dr} \qquad (1)$$

The proportionality constant η is known as the **coefficient of viscosity**, and is the quantity of interest. Thus η may be defined as the force per unit area required to move a layer of fluid with a velocity difference of 1 cm per second past another parallel layer 1 cm away. It is evident that the dimensions of η is $\text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$. The SI unit of η is $\text{kg} \cdot \text{m}^{-1} \cdot \text{sec}^{-1}$, and the CGS unit is $\text{gm} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$ or poise (denoted by P), and is equal to one-tenth the SI unit.

The theory of the process was first worked out by J. L. Poiseuille in 1844. Consider a fluid flowing through a tube of circular cross-section with radius R and length L. The fluid layer in the closest proximity of the walls is assumed to be stagnant, and the rate of flow increases to a maximum at the centre of the tube. Let v be the linear velocity at any distance r from the axis of the tube. A cylinder of fluid of radius r experiences a viscous drag given by Eq.(1) as

$$F_r = -\eta \frac{dv}{dr} \cdot 2\pi rL \tag{2}$$

For a steady flow, this force must be exactly balanced by the force driving the fluid in this cylinder through the tube. Since the pressure is the force per unit area, the driving force is

$$F_d = \pi r^2 (P_1 - P_2) \tag{3}$$

where P_1 and P_2 are fore and back pressures, respectively. Therefore, for steady flow, $F_r = F_d$, that is

$$-\eta \frac{dv}{dr} \cdot 2\pi rL = \pi r^2 (P_1 - P_2)$$

so that,

$$dv = -\frac{r}{2\eta L}(P_1 - P_2)dr \tag{4}$$

On integration of Eq.(4) we get

$$v = -\frac{(P_1 - P_2)r^2}{4\eta L} + \text{constant of integration} \tag{5}$$

According our hypothesis, $v = 0$, when $r = R$; this boundary condition determines the integration constant, so that

$$v = \frac{(P_1 - P_2)}{4\eta L}(R^2 - r^2) \tag{6}$$

The total volume of fluid flowing through the tube per second dV/dt is calculated by integrating the fluid velocity v over each element of cross-sectional area $2\pi rdr$. Thus,

$$\frac{dV}{dt} = \int_0^R 2\pi rv dr = \frac{\pi(P_1 - P_2)R^4}{8\eta L} \tag{7}$$

This is Poiseuille's equation which applies to incompressible fluids undergoing laminar flow. Poiseuille's equation may be satisfactorily applied to liquids but not to gases, as volume is a strong function of pressure for gases.

Under a constant pressure head $P = P_1 - P_2$, V volume of a liquid is allowed to flow through a fine capillary tube of known radius R. The length L and the time t for the flow are noted. The equation would thus be

$$\eta = \frac{\pi PR^4 t}{8LV} \tag{8}$$

Using the Ostwald viscometer one can measure the relative viscosity of a liquid, relative to the viscosity (known) of another liquid, referred to as the reference liquid. Therefore,

$$\frac{\eta_X}{\eta_{\text{H}_2\text{O}}} = \frac{\pi P_X R^4 t_X / 8LV}{\pi P_{\text{H}_2\text{O}} R^4 t_{\text{H}_2\text{O}} / 8LV} = \frac{P_X t_X}{P_{\text{H}_2\text{O}} t_{\text{H}_2\text{O}}} = \frac{hg\rho_X t_x}{hg\rho_{\text{H}_2\text{O}} t_{\text{H}_2\text{O}}}$$

Upon cancellation, we have

$$\frac{\eta_X}{\eta_{\text{H}_2\text{O}}} = \frac{\rho_X t_x}{\rho_{\text{H}_2\text{O}} t_{\text{H}_2\text{O}}} \tag{9}$$

If $\eta_{\text{H}_2\text{O}}$ is known, a measurement of the densities and times of flow of the two would yield η_X, the coefficient viscosity of the unknown liquid.

Procedure: *(Please do not report in your laboratory notebook)*

1. Rinse the Ostwald viscometer with distilled water and drain out the water thoroughly.
2. Add 10 ml of distilled water using a 10 ml pipette into the wider limb of the viscometer and clamp it vertically. Suck the water through the narrower limb of the viscometer and release it and start the stop-watch as the meniscus touches the upper mark of the bulb. Allow the water to flow and stop the stop-watch as the meniscus touches the lower mark of the bulb. Repeat the process twice, and calculate the average time of flow.
3. Remove the water completely from the viscometer and rinse it with a small amount of the supplied liquid 3%, discard the liquid after rinsing. Repeat step 2 with 3% and note down the time of flow.
4. Remove the 3% solution completely from the viscometer and rinse it with a small amount of water followed by a small amount of the supplied 6% solution; discard the liquid after rinsing. Repeat step 2 with 6% and note down the time of flow.
5. Repeat steps 2, 3, and 4 with the 9% and 12% solutions, and the solution marked X.
6. Using a clean and dry specific gravity bottle determine the specific gravities of the supplied solutions (3%, 6%, 9%, 12% and X).
7. Calculate the relative viscosity coefficient ratios and the relative viscosity coefficients of the supplied solutions (3%, 6%, 9%, 12% and X).
8. Plot the concentrations in % (along X axis) and the viscosity coefficient values (along Y axis) and draw a free-hand curve. From the value of the viscosity coefficient of the solution marked X, determine its concentration.

Results and Calculations:

1. Experimental temperature: …… °C
   Given: Density of water at …… °C = …… g/ml.
   Coefficient of viscosity of water at …… °C = …… poise.
2. Determination of the specific gravities:

Sl. No.	Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
1	Empty		×	×	×
2	Water				
3	3% solution				
4	6% solution				
5	9% solution				
6	12% solution				
7	X% solution				

3. Determination of the relative surface tension ratios (γ_X/γ_{H_2O}):

Sl. No.	Substance	No. of Obs.	Time of flow (s)	Mean time of flow (s)	Relative viscosity ratio (η_X/η_{H_2O})
1.	Water	1.			
		2.			
		3.			
2.	3%	1.			
		2.			
		3.			
3.	6%	1.			
		2.			
		3.			
4.	9%	1.			

		2.			
		3.			
5.	12%	1.			
		2.			
		3.			
6.	X%	1.			
		2.			
		3.			

Conclusion: From the graph, the concentration of the solution with unknown concentration has been determined to be …… %, respectively at …… °C.

SEMESTER – II
(UNDER THE CCFUP, NEP 2020)
[FOR HONOURS MINOR, PAPER: CEMMI02P]

Experiment 1: To determine the rate constant of decomposition of H_2O_2 by acidified KI solution using the clock reaction.

Theory: In dilute acid medium (like dilute H_2SO_4), H_2O_2 reacts with KI according to

$$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + 2H_2O + K_2SO_4$$

Ionically,

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

Suppose that at $t = 0$, the concentration of H_2O_2 is a, and that after some time t has elapsed the concentration of H_2O_2 becomes $a - x$, the concentration of liberated I_2 is x (its initial concentration being zero). The overall reaction is kinetically of second order, being first order in $[H_2O_2]$ and first order in $[I^-]$. The rate of the reaction may be expressed according to

$$\text{rate} = -\frac{d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

where, k is the second order rate constant, and [ ]'s represents the molar concentrations of the species. The unit of k is $(\text{mol/lit})^{-1}(\text{time})^{-1}$.

The reaction actually occurs in two steps:

$$H_2O_2 + I^- \xrightarrow{\text{slow}} H_2O + OI^-$$
$$IO^- + 2H^+ + I^- \xrightarrow{\text{fast}} H_2O + I_2$$

The first step is the rate-determining step.

If the iodide ion concentration, $[I^-]$, is kept constant, in large excess, the reaction becomes kinetically of pseudo first order in $[H_2O_2]$. This condition is achieved by adding sodium thiosulfate solution continuously in small amounts to the reaction mixture, when thiosulfate ions react with the liberated iodine and regenerate iodide according to

$$I_2 + 2S_2O_3^{2-} = S_4O_6^{2-} + 2I^-$$

Under these conditions the rate equation is transformed to

$$-\frac{d[H_2O_2]}{dt} = k_1[H_2O_2]$$

where, k_1 is the pseudo first order rate constant of the reaction. Integrating the above equation with the boundary conditions at $t = 0$, $[H_2O_2] = a$; at $t = t$, $[H_2O_2] = a - x$, where, x is the amount of H_2O_2 reacted (which in turn is the equivalent of liberated iodine, or the equivalent of thiosulfate consumed), one obtains

$$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$$

If V_0 is the titre value of thiosulfate for iodine liberated by a fixed volume, say 10 ml, of H_2O_2 solution (this is equivalent to the initial concentration of H_2O_2, that is a), and $V_t$is the titre value of the same thiosulfate solution for the iodine liberated by the same volume (10 ml) of H_2O_2 present in the reaction mixture (undergoing reaction) at time t (this is equivalent to x), then substituting for a and $a - x$ in the above rate equation one obtains the working equation

$$k_1 = \frac{2.303}{t}\log_{10}\frac{V_0}{V_0 - V_t}$$

$$\therefore \log_{10}\frac{V_0}{V_0 - V_t} = \frac{k_1}{2.303}t$$

A plot of $\log_{10}\frac{V_0}{V_0 - V_t}$ against t will be a straight line of slope $\frac{k_1}{2.303}$ and passing through the origin. k_1 may be evaluated from the slope.

Procedure:

1. Prepare an approximately (N/10) sodium thiosulfate solution.
2. Fill the burette with the ~(N/10) sodium thiosulfate solution.
3. Using a measuring cylinder take 10 ml of the supplied 1:2 H_2SO_4 in a 500 ml conical flask. Add 2 gm of solid KI and 50 ml of distilled water. Then using a 10 ml pipette add the supplied H_2O_2 solution. Cover the mouth of the conical flask with a watch glass and keep in dark (preferably inside your cupboard) for 15 minutes. Remove from the dark, add 100 ml of distilled water and titrate the liberated iodine with the sodium thiosulfate solution using starch solution as indicator (note that, add starch solution once the solution is straw yellow in color, and not before when the solution is intense red). Record the titer value. This is V_0.
4. Take 250 ml of the supplied KI solution in a 500 ml conical flask. Add 15 ml of the supplied 1:2 H_2SO_4 and 5 ml of freshly prepared starch solution. Add 10 ml of the supplied H_2O_2 solution into the mixture using a pipette and start the stopwatch at the time of half discharge. Homogenize the reaction mixture, a blue color will appear. Discharge the blue color by adding excess of ~(N/10) thiosulfate solution immediately. Wait for the reappearance of blue color and record the time of reappearance of color. The volume of thiosulfate consumed will correspond to the time of reappearance of the blue color. Take at least 7 readings. The values of the volumes of ~(N/10) thiosulfate solution that you have added successively correspond to V_t.
5. Using these experimental data, determine k graphically.

Results and Calculations:

1. Temperature of the experiment: ……. ℃.
2. Titration of H_2O_2 using the supplied sodium thiosulphate solution: $V_0 =$ …….. ml.
3. Kinetic data for the clock reaction:

Obs.	Clock Time (min)	t_n (min)	V_n (ml)	$\log_{10}[V_0/(V_0 - V_n)]$

4. Plotted $\log_{10}[V_0/(V_0 - V_n)]$ (along the Y axis) versus t_n (along the X axis). From the slope of the graph the rate constant k was determined to be …… minute^{-1}.

Conclusion: The rate constant of decomposition of H_2O_2 by acidified KI solution using the clock reaction was determined to be …… minute^{-1}.

Experiment 2: To determine the rate constant of the first order acid catalyzed hydrolysis of an ester titrimetrically.

Theory: The rate of a first order reaction is directly proportional to the first power of the concentration of the reactant. A first order reaction may be represented as,

$$A \rightarrow \text{Products}$$

for which the rate,

$$-\frac{dC_A}{dt} = kC_A$$

where, k, is the rate constant (having a dimension of time^{-1}) and C_A is the molar concentration of A at time t. Integration of the above rate equation with proper limits at $t = 0, C_A = C_0$ and $t = t, C_A = C_t$, converting the logarithmic term to base 10 (that is, $\log_{10}$) one obtains,

$$k = \frac{2.303}{t}\log_{10}\left(\frac{C_0}{C_t}\right)$$

Hydrolysis of an ester (R^1COOR^2), although appears to be bimolecular, but it is kinetically a first order reaction with respect to the ester, since, water molecules are present in large excess.

$$R^1COOR^2 + H \cdot OH \xrightarrow{H^+} R^1COOH + R^2OH$$

The reaction is slow and is efficiently catalyzed by strong acids (say HCl, H^+ being the active ion). When a known amount of the ester (say methyl acetate/ethyl acetate) is allowed to hydrolyze in the presence of a known amount of strong acid (say HCl), the progress of the reaction may be studied by withdrawing measured volumes of aliquots from the reaction mixture at different intervals of time and titrating the same with a standard alkali (say NaOH) solution using phenolphthalein as indicator. The volume of standard alkali required for a known volume of the aliquot at any instant of time is equivalent to the sum of the amount of acetic acid (a weak acid) formed and the amount of strong acid used as the catalyst (a fixed amount). If V_0, V_t and V_∞ be the volumes of the standard alkali required for the same volume of the aliquots at the beginning ($t = 0$), at the instant t and at the end of the reaction (infinite time, $t = \infty$), then

$(V_\infty - V_0) \equiv C_0$, the initial amount of the ester

$(V_t - V_0) \equiv$ amount of ester consumed $=$ amount of weak acid formed

$(V_\infty - V_0) - (V_t - V_0) \equiv (V_\infty - V_t) \equiv C_t =$ amount of ester left

$$\therefore k = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

$$\therefore \log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right) = \left(\frac{k}{2.303}\right)t$$

Thus, measuring V_0, V_t and V_∞ and plotting $\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$ against t, it is possible to determine k from the slope of the resulting straight line passing through the origin.

$$k = 2.303 \times \text{slope}$$

Note: The experimentally determined rate constant k is related to the concentration $[H^+]$ of the acid (catalyst) according to $k = k_0[H^+]$, k_0 being the rate constant of the uncatalyzed reaction.

Procedure: (*Please do not report in your laboratory notebook*)

1. Prepare about 250 ml of ~(N/10) NaOH solution in a glass bottle.
2. Fill up a clean burette with the ~(N/10) NaOH solution.
3. Take approximately 250 ml of distilled water in a 500 ml conical flask, and add 1-2 drop(s) of phenolphthalein indicator solution.
4. Take 50 ml of the supplied catalyst solution (by pipetting out twice using a 25 ml pipette) in a 100 ml dry conical flask. Add 5 ml of the supplied ester to the catalyst solution and note the time of half discharge. Mix the solution thoroughly.
5. Withdraw a 2 ml aliquot from the reaction mixture into the 500 ml conical flask containing 250 ml distilled water. Note down the time of half discharge. Titrate the solution using the ~(N/10) NaOH solution and record the titre value as V_1 against the time t_1.

6. Repeat step 5 at 4-5 minutes intervals and record the titre values as V_n against the times t_n.
7. Allow the reaction mixture to reflux at 60 °C using air condenser for 45 minutes. Allow it to cool down to room temperature.
8. Titrate 2 ml of the refluxed solution against the ~(N/10) NaOH solution and record the titre value as V_∞.
9. Using the experimental data, determine the value of k graphically.

Results and Calculations:

1. Experimental temperature:

Temperature before expt. (°C)	Temperature after expt. (°C)	Mean temperature (°C)

2. Preparation of 250 ml approximately (N/10) NaOH solution: ____ number of half beads of NaOH were dissolved in approximately 250 ml distilled water, followed by a thorough homogenization to prepare approximately (N/10) NaOH solution.
3. Preparation of reaction mixture: To 50 ml of the supplied catalyst solution taken in a 100 ml conical flask 5 ml of the supplied ester was added, the stopwatch was started at the half discharge from the 5 ml pipette, and the mixture was thoroughly homogenized.
4. Kinetic data:

No. of Obs.	Time (t_n) (min)	Titre value (V_n) (ml)
1	(t_1)	(V_1)
2		
3		
4		
5		
6		
7		
8		
9		

5. Determination of V_∞: 2 ml of the refluxed solution was titrated against the ~(N/10) NaOH solution and the titre value was recorded to be _____ ml.
6. Table for graph:

No. of Obs.	$\Delta t_n = t_n - t_1$ $(n > 1)$ (min)	$\frac{V_\infty - V_1}{V_\infty - V_n}$	$\log_{10}\left(\frac{V_\infty - V_1}{V_\infty - V_n}\right)$
1			
2			
3			
4			
5			
6			
7			
8			

7. From the plot of $\log_{10}\left(\frac{V_\infty - V_1}{V_\infty - V_n}\right)$ against Δt_n, the slope was determined to be _____ min^{-1}.
8. The pseudo first order rate constant, k was found to be _____ min^{-1} at ____ °C.

Conclusion: The pseudo first order rate constant, k was found to be _____ min^{-1} at ____ °C.

Experiment 3: To study the kinetics of the reaction between $K_2S_2O_8$ and KI.

Theory: The rate of the reaction

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

depends most likely on the slow second order bimolecular reaction

$$I^- + (S_2O_8I)^{3-} \rightarrow I_2 + 2SO_4^{2-}$$

The second order reaction rate is given by

$$\frac{dx}{dt} = k[S_2O_8^{2-}][I^-] = k(a-x)(b-x)$$

If the initial concentrations of $S_2O_8^{2-}$ and I^- ions are expressed in normality, instead of molarity, and if for simplicity the initial concentrations of both the reactants are equal, that is, $a = b$, the above equation reduces to

$$\frac{dx}{dt} = k(a-x)^2$$

which on integration within appropriate limits gives

$$k = \frac{1}{t}\frac{x}{a(a-x)}$$

Thus, the reaction rate can be followed by measuring the rate of liberation of I_2 along with the knowledge of the initial concentrations of the reactants. If now $x/(a-x)$ is plotted against t (measured from the time of mixing of the reactants) a straight line is obtained which passes through the origin. The rate constant k can be determined from the slope of the straight line as $k = \text{slope}/a$. The order of the reaction may be determined by performing the experiment with two different initial concentrations a_1 and a_2. Thus, by noting the times for consumption $t_1$and t_2 of a particular fraction of the reactants in the two cases, one has

$$t_1/t_2 = (a_2/a_1)^{n-1}$$

where n is the order of the reaction. Therefore,

$$n = 1 + \frac{\log(t_1/t_2)}{\log(a_2/a_1)}$$

Procedure:

1. Note down the room temperature.
2. Prepare 100 ml of standard (N/10) $K_2Cr_2O_7$ solution.
3. Prepare approximately 250 ml of approximately (N/10) $Na_2S_2O_3$ solution.
4. Standardize the approximately (N/10) $Na_2S_2O_3$ solution using the standard (N/10) $K_2Cr_2O_7$ solution iodometrically.
5. Quantitatively dilute the (N/10) $Na_2S_2O_3$ solution to (N/100) $Na_2S_2O_3$ solution.
6. Prepare 250 ml of approximately (>N/10) (slightly higher) $K_2S_2O_8$ solution.
7. Standardize the (>N/10) (slightly higher) $K_2S_2O_8$ solution using the following procedure: Pipette out 10 ml of (>N/10) (slightly higher) $K_2S_2O_8$ solution in a 500 ml conical flask, add 10 ml of 10% (w/v) KI solution and 2 ml of glacial acetic acid. Cover the conical flask with a watch glass and keep the mixture in dark for 30 minutes. Add 80 ml distilled water and then titrate the liberated iodine with the standardized $Na_2S_2O_3$ solution of order (N/10) using starch indicator. Calculate the strength of the $K_2S_2O_8$ solution. Prepare an exact (N/10) $K_2S_2O_8$ solution by exact quantitative dilution of the standardized solution.
8. Prepare 250 ml of approximately (>N/10) (slightly higher) KI solution. Quantitatively dilute this solution to prepare exactly (N/10) KI solution.
9. Prepare an exact 0.75(N) KCl solution.
10. Prepare the following sets (one-by-one):

Set	Volume (in ml) of				
	(N/10) $K_2S_2O_8$ solution	**(N/10) KI solution**	**0.75 (N) KCl solution**	**Water**	**Total**
I	50.0	50.0	0.0	0.0	100.0
II	25.0	25.0	0.0	50.0	100.0

11. For each set, the initial time (the time at which the stopwatch is started) is noted just at the time of half-discharge of the exact (N/10) KI solution to the exact (N/10) $K_2S_2O_8$ solution. Take 10 ml aliquot from each of the sets after an interval of 2 minutes initially, followed by an interval of 3-4 minutes after the reaction has progressed to some extent. Titrate the aliquot with the exact (N/100) $Na_2S_2O_3$ solution using starch solution as an indicator.
12. Draw the straight lines for all the sets on a single graph paper using different symbols for points of different sets. Then find the slopes for each of the line and calculate the corresponding rate constants.
13. Use the data corresponding to Sets I and II to draw graphs of x versus t. Note the t_1 for a particular volume x_1 for Set-I and t_2 for the volume $x_2 = x_1/2$ for the second set and use these t's for the calculation of the order of reaction noting that $a_1 = \mathrm{N}/20$ and $a_2 = \mathrm{N}/40$ after mixing the reactants.

Results and Calculations:

1. Experimental temperature: _____ °C.
2. Weight of $K_2Cr_2O_7$ taken = _____ gm. Hence, the strength of $K_2Cr_2O_7$ solution is ……(N).
3. Standardization of the $Na_2S_2O_3$ solution: Volume of $K_2Cr_2O_7$ solution pipetted out = 25 ml

Obs.	Burette reading		Volume of $Na_2S_2O_3$ (ml)	Mean volume of $Na_2S_2O_3$ (ml)	Strength of $Na_2S_2O_3$
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

4. Weight of KI taken = _____ gm. Hence, the strength of KI solution is ……(N).
5. Weight of $K_2S_2O_8$ taken in a rough balance = _____ gm.
6. Weight of $Na_2S_2O_3$ taken in a rough balance = _____ gm.
7. Standardization of the $K_2S_2O_8$ solution: Volume of $Na_2S_2O_3$ solution consumed = ……. ml. Hence, the strength of $K_2S_2O_8$ solution is …… (N).
8. Quantitative dilution of the $K_2S_2O_8$ solution: …… ml of the …… (N) $K_2S_2O_8$ solution was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water to prepare 100 ml exactly 0.1 (N) $K_2S_2O_8$ solution.
9. Quantitative dilution of the KI solution: …… ml of the …… (N) KI solution was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water to prepare 100 ml exactly 0.1 (N) KI solution.
10. Preparation of sets (one at a time for the kinetic study):

Set	(N/10) KI solution (ml)	(N/10) $K_2S_2O_8$ solution (ml)	Water (ml)
I	50.0	50.0	0.0
II	25.0	25.0	50.0

11. Kinetic data for Set-I: [50 ml (N/10) KI + 50 ml (N/10) $K_2S_2O_8$] and Set-II: [25 ml (N/10) KI + 25 ml (N/10) $K_2S_2O_8$]

Set-I: [50 ml (N/10) KI + 50 ml (N/10) $K_2S_2O_8$]		Set-II: [25 ml (N/10) KI + 25 ml (N/10) $K_2S_2O_8$]	
t (minutes)	Titer value, V_t (ml)	t (minutes)	Titer value, V_t (ml)
1		1	
2		2	
3		3	
4		4	
⋮		⋮	

12.Plotted x against t to determine k_1 and k_2 for both the Sets I and II, respectively.

For Set-I, $k_1 =$..... $\text{lit equiv}^{-1}\text{minute}^{-1}$.

For Set-II, $k_2 =$..... $\text{lit equiv}^{-1}\text{minute}^{-1}$.

Ratio, $k_1/k_2 =$ .....

Conclusion: The rate constants were determined to be ..... and ..... $\text{lit equiv}^{-1}\text{minute}^{-1}$ for the two sets, and their ratio was found to be .....

SEMESTER – III

(UNDER THE CBCS PATTERN)

Experiment 1: Determination of the relative viscosity ratio and the relative viscosity coefficients of liquids or dilute solutions using an Ostwald's viscometer.

Theory: The concept of viscosity is usually met in problems of fluid flow, treated by hydrodynamics, as a measure of the fractional resistance that a fluid in motion offers to an applied shearing force. If a fluid is flowing past a stationary plane surface, the layer of fluid adjacent to the plane boundary is stagnant; successive layers have increasingly higher velocities. The frictional force, F, resisting the relative motion of any two adjacent layers, is proportional to the area of interface, S between them and to the velocity gradient, dv/dr between them. This is known as the Newton's law of viscous flow, and is applicable to nonconservative/dissipative systems only. Thus,

$$F \propto S\frac{dv}{dr} \Rightarrow F = \eta S\frac{dv}{dr} \tag{1}$$

The proportionality constant η is known as the **coefficient of viscosity**, and is the quantity of interest. Thus η may be defined as the force per unit area required to move a layer of fluid with a velocity difference of 1 cm per second past another parallel layer 1 cm away. It is evident that the dimensions of η is $\text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$. The SI unit of η is $\text{kg} \cdot \text{m}^{-1} \cdot \text{sec}^{-1}$, and the CGS unit is $\text{gm} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$ or poise (denoted by P), and is equal to one-tenth the SI unit.

The theory of the process was first worked out by J. L. Poiseuille in 1844. Consider a fluid flowing through a tube of circular cross-section with radius R and length L. The fluid layer in the closest proximity of the walls is assumed to be stagnant, and the rate of flow increases to a maximum at the centre of the tube. Let v be the linear velocity at any distance r from the axis of the tube. A cylinder of fluid of radius r experiences a viscous drag given by Eq.(1) as

$$F_r = -\eta\frac{dv}{dr} \cdot 2\pi rL \tag{2}$$

For a steady flow, this force must be exactly balanced by the force driving the fluid in this cylinder through the tube. Since the pressure is the force per unit area, the driving force is

$$F_d = \pi r^2(P_1 - P_2) \tag{3}$$

where P_1 and P_2 are fore and back pressures, respectively. Therefore, for steady flow, $F_r = F_d$, that is

$$-\eta\frac{dv}{dr} \cdot 2\pi rL = \pi r^2(P_1 - P_2)$$

so that,

$$dv = -\frac{r}{2\eta L}(P_1 - P_2)dr \tag{4}$$

On integration of Eq.(4) we get

$$v = -\frac{(P_1 - P_2)r^2}{4\eta L} + \text{constant of integration} \tag{5}$$

According our hypothesis, $v = 0$, when $r = R$; this boundary condition determines the integration constant, so that

$$v = \frac{(P_1 - P_2)}{4\eta L}(R^2 - r^2) \tag{6}$$

The total volume of fluid flowing through the tube per second dV/dt is calculated by integrating the fluid velocity v over each element of cross-sectional area $2\pi rdr$. Thus,

$$\frac{dV}{dt} = \int_0^R 2\pi rvdr = \frac{\pi(P_1 - P_2)R^4}{8\eta L} \quad (7)$$

This is Poiseuille's equation which applies to incompressible fluids undergoing laminar flow. Poiseuille's equation may be satisfactorily applied to liquids but not to gases, as volume is a strong function of pressure for gases.

Under a constant pressure head $P = P_1 - P_2$, V volume of a liquid is allowed to flow through a fine capillary tube of known radius R. The length L and the time t for the flow are noted. The equation would thus be

$$\eta = \frac{\pi PR^4 t}{8LV} \quad (8)$$

Using the Ostwald viscometer one can measure the relative viscosity of a liquid, relative to the viscosity (known) of another liquid, referred to as the reference liquid. Therefore,

$$\frac{\eta_X}{\eta_{\mathrm{H_2O}}} = \frac{\pi P_X R^4 t_X/8LV}{\pi P_{\mathrm{H_2O}} R^4 t_{\mathrm{H_2O}}/8LV} = \frac{P_X t_X}{P_{\mathrm{H_2O}} t_{\mathrm{H_2O}}} = \frac{hg\rho_X t_x}{hg\rho_{\mathrm{H_2O}} t_{\mathrm{H_2O}}}$$

Upon cancellation, we have

$$\frac{\eta_X}{\eta_{\mathrm{H_2O}}} = \frac{\rho_X t_x}{\rho_{\mathrm{H_2O}} t_{\mathrm{H_2O}}} \quad (9)$$

If $\eta_{\mathrm{H_2O}}$ is known, a measurement of the densities and times of flow of the two would yield η_X, the coefficient viscosity of the unknown liquid.

Procedure: *(Please do not report in your laboratory notebook)*

1. Rinse the Ostwald viscometer with distilled water and drain out the water thoroughly.
2. Add 10 ml of distilled water using a 10 ml pipette into the wider limb of the viscometer and clamp it vertically. Suck the water through the narrower limb of the viscometer and release it and start the stop-watch as the meniscus touches the upper mark of the bulb. Allow the water to flow and stop the stop-watch as the meniscus touches the lower mark of the bulb. Repeat the process twice, and calculate the average time of flow.
3. Remove the water completely from the viscometer and rinse it with a small amount of the supplied liquid VA, discard the liquid after rinsing. Repeat step 2 with VA and note down the time of flow.
4. Remove the solution VA completely from the viscometer and rinse it with a small amount of water followed by a small amount of the supplied liquid VB; discard the liquid after rinsing. Repeat step 2 with VB and note down the time of flow.
5. Using a clean and dry specific gravity bottle determine the specific gravities of the supplied solutions VA and VB.
6. Calculate the relative viscosity ratios and the relative viscosity coefficients of VA and VB.

Results and Calculations:

1. Experimental temperature: …… °C
   Given: Density of water at **……** °C = **……** g/ml.
   Coefficient of viscosity of water at **……** °C = **……** poise.
2. Determination of the specific gravities:

Sl. No.	Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
1	Empty		×	×	×
2	Water				

3	Solution-A (VA)				
4	Solution-B (VB)				

3. Determination of the relative viscosity ratios (η_X/η_{H_2O}):

Sl. No.	Substance	No. of Obs.	Time of flow (s)	Mean time of flow (s)	Relative viscosity ratio (η_X/η_{H_2O})
1.	Water	1.			
		2.			
		3.			
2.	Solution-A (VA)	1.			
		2.			
		3.			
3.	Solution-B (VB)	1.			
		2.			
		3.			

Conclusion: The relative viscosity ratios of the liquids VA and VB are …… and ……, and the relative viscosity coefficients are …… poise and …… poise, respectively at …… °C.

Experiment 2: To determine the partition coefficient of molecular iodine between water and an organic solvent ($\mathbf{CCl_4/CHCl_3}$).

Theory: If a solute, say S, is added in a system containing two immiscible liquids α and β, and if the solute is soluble in both the liquids, then it distributes itself between the two liquids in a definite manner, such that

$$S(\alpha) = S(\beta) \tag{1}$$

and

$$\frac{C_\alpha}{C_\beta} = K_D \tag{2}$$

where C_α and C_β are the equilibrium molar concentrations of the solute in the two liquids and K_D is a constant (at a constant temperature) known as the **distribution coefficient** or the **partition coefficient**. The above behaviour is a consequence of the thermodynamic requirements for equilibrium. To demonstrate this, we consider a pair of immiscible solvents, α and β in contact, both containing the same substance in solution. The chemical potential of the solute in liquid α, μ_α can be represented by

$$\mu_\alpha = \mu_\alpha^\circ + RT \ln a_\alpha \tag{3}$$

where μ_α° is the standard chemical potential and a_α the activity of the solute in solvent α. Similarly, the chemical potential of the solute in the second liquid, μ_β, can be written as

$$\mu_\beta = \mu_\beta^\circ + RT \ln a_\beta \tag{4}$$

where all the quantities bear the same significance as in Eq. (3), except that they now refer to liquid β. Since for an equilibrium between two layers we must have $\mu_\alpha = \mu_\beta$ at constant temperature and pressure, it follows that

$$\mu_\beta^\circ + RT \ln a_\beta = \mu_\alpha^\circ + RT \ln a_\alpha$$

so that,

$$\ln \frac{a_\beta}{a_\alpha} = \frac{\mu_\alpha^\circ - \mu_\beta^\circ}{RT}.$$

However, at any given temperature μ_α° and μ_β° are constants for a given substance in the particular solvents. Hence,

$$\ln \frac{a_\beta}{a_\alpha} = \text{constant}, \text{so that}, \frac{a_\beta}{a_\alpha} = \text{constant} = K \tag{5}$$

The above equation is a mathematical statement of the **Nernst distribution law**, which states that a substance will distribute itself between two solvents until at equilibrium the ratio of the activities of the substance in the two layers is constant at any given temperature. When the solutions are dilute, or when the solute behaves ideally, the activity is essentially equal to the concentration C, and Eq. (5) reduces to Eq. (2). The constant K_D is the partition coefficient of the solute between the two solvents. The distribution law will be strictly valid provided

(a) the solutions are ideal and dilute,
(b) the presence of the solute does not alter the mutual solubility of the two layers, and
(c) the solute has the same molar mass in both the layers, that is, there is neither any association, nor there is dissociation.

As an application of this general rule, we observe that when water is added to a solution of I_2 in CCl_4 or $CHCl_3$, I_2 distributes itself in both the aqueous and CCl_4 or $CHCl_3$ layers after some time. The partition coefficient of I_2, at the equilibrium state and at a constant temperature, between CCl_4 or $CHCl_3$ and water is given by

$$K_D = \frac{\text{Concentration of } I_2 \text{ in } CCl_4 \text{ or } CHCl_3 \text{ layer}}{\text{Concentration of } I_2 \text{ in aqueous layer}} = \frac{C^{(I_2)}_{CCl_4/CHCl_3}}{C^{(I_2)}_{H_2O}} \qquad (6)$$

Procedure: *(Please do not report in your laboratory notebook)*

1. Record the room temperature.
2. Using the supplied solution of I_2 in CCl_4 or $CHCl_3$ prepare the following sets

Set	Vol. of satd. soln. in CCl_4 / $CHCl_3$ (ml)	Vol. of pure CCl_4 / $CHCl_3$ (ml)	Vol. of water (ml)	Total vol. (ml)
I	30.0	0.0	120.0	150.0
II	25.0	5.0	120.0	150.0

3. Pipette out 25 ml of the aqueous layer and titrate with 0.02(N) $Na_2S_2O_3$ solution.
4. Pipette out 5 ml of the organic layer and titrate with 0.1(N) $Na_2S_2O_3$ solution.

Results and Calculations:

1. Temperature of the experiment: … °C
2. About 20 gm of resublimed I_2 was taken in a 250 ml stoppered bottle, 100 ml of CCl_4 or $CHCl_3$ was added to it. The bottle was tightly stoppered and then shaken for 45 minutes to prepare a saturated solution of I_2 in CCl_4 or $CHCl_3$. The solution was then filtered into a dry bottle through glass wool.
3. Composition of sets:

Set	Vol. of satd. soln. in CCl_4 / $CHCl_3$ (ml)	Vol. of pure CCl_4 / $CHCl_3$ (ml)	Vol. of water (ml)	Total vol. (ml)
I	30.0	0.0	120.0	150.0
II	25.0	5.0	120.0	150.0

4. Partition coefficient of I_2 between water and CCl_4 or $CHCl_3$:

25 ml of the aqueous layer titrated with 0.02(N) $Na_2S_2O_3$ solution.
5 ml of the CCl_4 / $CHCl_3$ layer titrated with 0.1(N) $Na_2S_2O_3$ solution.
[Neither 0.02(N) nor 0.1(N) solutions of $Na_2S_2O_3$ be standardized, since K_D is a ratio of two concentration terms.]

Set	Layer	Obs.	Burette reading		Vol. of thiosulphate (ml)	Mean vol. (ml)	K_D	Mean K_D
			Initial	Final				
I	Aqueous	1.						
		2.						
		3.						
	Organic	1.						

		2.						
		3.						
II	Aqueous	1.						
		2.						
		3.						
	Organic	1.						
		2.						
		3.						

Now, 25 ml of aqueous layer $\equiv V_{H_2O}$ ml of 0.02(N) $Na_2S_2O_3$ solution. And 5 ml of CCl_4 / $CHCl_3$ layer $\equiv V_{CCl_4\ /\ CHCl_3}$ ml of 0.1(N) $Na_2S_2O_3$ solution. Thus, 5 ml of CCl_4 / $CHCl_3$ layer $\equiv 5 \times V_{CCl_4\ /\ CHCl_3}$ ml of 0.02(N) $Na_2S_2O_3$ solution.

Therefore, 25 ml of CCl_4 / $CHCl_3$ layer $\equiv 5 \times 5 \times V_{CCl_4\ /\ CHCl_3}$ of 0.02(N) $Na_2S_2O_3$ solution.

$$\therefore K_D = \frac{25 \times \text{titre value with } 0.1\ (\text{N})Na_2S_2O_3 \text{ solution}}{\text{titre value with } 0.02\ (\text{N})Na_2S_2O_3 \text{ solution}}$$

$$\therefore K_D(\text{Set} - \text{I}) = \frac{\times}{} = \quad \text{and} \quad K_D(\text{Set} - \text{I}) = \frac{\times}{} =$$

$$\therefore \text{Mean } K_D = \frac{+}{} = \text{ at}$$

Experiment 3: To determine the concentration of a strong monobasic acid by conductometric titration using a standardized NaOH solution.

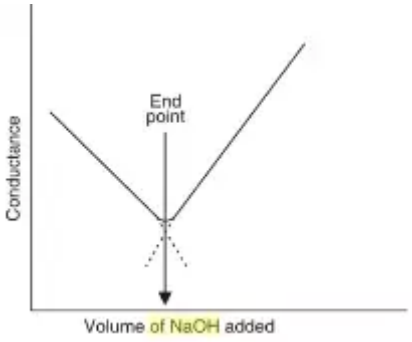
Theory: The specific conductance, κ, of an electrolytic solution depends upon the concentration of the electrolyte, charges of the ions, and their mobilities and may be expressed as

$$\kappa = \text{constant} \times \sum_i c_i u_i$$

where c_i is the concentration of the ith ion in g ion/liter, and u_i is its mobility. The constant includes the absolute values of charges. Thus, for a solution of HCl in water

$$\kappa = \text{constant}[c_{H^+}u_{H^+} + c_{Cl^-}u_{Cl^-}] = \text{constant} \cdot c_{HCl}[u_{H^+} + u_{Cl^-}]$$

since water is practically unionized and since $c_{H^+} = c_{Cl^-} = c_{HCl}$. As the strong acids are completely ionized, the initial conductance of HCl will be high. When a small amount (say x mol) of the strong base (say NaOH) is added, the highly conducting H^+ ions of the completely ionized strong acid are replaced by Na^+ ions having much lower conductance. As a result, the conductance of the solution decreases, since the H^+ ion and OH^- ion combine to form unionized H_2O molecules ($H^+ + OH^- \rightleftharpoons H_2O$). Immediately after the equivalence point, the conductance, κ, of the solution shows a rise, since the conducting power of OH^- ions (from the excess NaOH) is much higher than that of the Cl^- ions. If z moles of the base are added after the complete neutralization of the acid, the solution will contain Na^+, Cl^- and OH^- ions. This indicates that the plot of κ versus the number of moles of NaOH, z, will be a straight line with positive slope. Since $u_{OH^-} \gg u_{Cl^-}$, the slope of this line will be greater than that of κ' versus the moles of NaOH (y). Thus, the decrease in conductance will be steeper than the corresponding increase in conductance after the neutralization point is crossed. Volume change during the titration will be almost negligible if the concentration of the titrant is 5-10 times as the concentration of the acids. Under this condition the plot of specific conductance versus the volume (or the number of drops) of the titrant added for a particular neutralization will almost be a straight line. The resulting plot will consist of two straight lines, mutually intersecting at an equivalence point.



Procedure: *(Please do not report in your laboratory notebook)*

1. Prepare 100 ml of an exact (N/10) oxalic acid solution (0.630 gm in 100 ml).
2. Prepare 100 ml of an approximately (N/2) NaOH solution by counting the no. of half beads.
3. Standardize the approximately (N/2) NaOH solution and calculate its exact strength.
4. In a 100 ml beaker pipette out 10 ml of the strong acid solution, add sufficient quantity of distilled water so as to immerse the conductivity cell, and note the initial value of the conductance.
5. Fill a 50 ml burette with the standard (N/2) NaOH solution, and calibrate the drop volume by allowing 1 ml of the solution to flow as drops and counting the no. of drops. Calculate the volume of one drop of NaOH solution flowing from the burette.
6. Add two drops of the NaOH solution from the burette to the test solution, homogenize properly, and note the conductance value.
7. Repeat step 6 till the equivalence point is reached and after that take 6-8 additional readings.
8. Plot the conductance versus no. of drops graph and from the intersection point of the two straight lines determine the exact equivalence point.

Results and Calculations

1. Experimental temperature: … ℃.

2. Preparation of 100 ml standard (N/10) oxalic acid solution: … gm of oxalic acid was accurately weighed in an electronic balance and was subsequently dissolved in 100 ml distilled water to prepare a … (N/10) oxalic acid solution.

3. Volume associated with 50 drops of the supplied $\sim NaOH$ solution: … ml.

∴ The volume of 1 drop of $NaOH$ solution: … ml.

4. Standardization of the supplied approximately (N/2) $NaOH$ solution: Volume of oxalic acid solution pipetted out = 25 ml

Obs.	Burette reading		Vol. of $NaOH$ required (ml)	Mean volume of $NaOH$ required (ml)	Strength of $NaOH$ (N)
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

5. Conductometric titration of the supplied strong acid: 10 ml of the supplied acid taken.

Obs.	Drop No.	Total Drop	C (μS)	Obs.	Drop No.	Total Drop	C (μS)
1.				11.			
2.				12.			
3.				13.			
4.				14.			
5.				15.			
6.				16.			
7.				17.			
8.				18.			
9.				19.			
10.				20.			

6. Data for graph:

Obs.	Total Drop	C (μS)	Obs.	Total Drop	C (μS)
1.			12.		
2.			13.		
3.			14.		
4.			15.		
5.			16.		
6.			17.		
7.			18.		
8.			19.		
9.			20.		
10.			21.		
11.			22.		

Conclusion: From the graph, no. of drops needed for neutralization is 46 drops, so that the corresponding volume is … ml. Hence, the strength of strong acid is … (N).

Experiment 4: To determine the equilibrium constant of the reaction $\mathbf{KI + I_2 \rightleftharpoons KI_3}$ by the partition method.

Theory: In aqueous solution iodine (I_2) reacts with potassium iodide (KI) to produce potassium tri-iodide (KI_3) according to $\mathrm{KI + I_2 \rightleftharpoons KI_3}$, for which the equilibrium constant K is given by

$$K = \frac{\left(a_{I_3^-}\right)_w}{(a_{I^-})_w \left(a_{I_2}\right)_w}$$

where the subscript *w* stands for aqueous solution. For dilute solutions the activities are very close to the molar concentrations, as the activity coefficients approach unity, and the equilibrium constant K may be expressed in terms of the molar concentration C according to:

$$K = \frac{\left(C_{I_3^-}\right)_w}{(C_{I^-})_w \left(C_{I_2}\right)_w}$$

The equilibrium concentration of I_2 in aqueous solution, $\left(C_{I_2}\right)_w$, may be obtained from the partition coefficient (K_d) by the application of the Nernst distribution law:

$$K_d = \frac{\left(C_{I_2}\right)_o}{\left(C_{I_2}\right)_w}$$

where the subscript *o* stands for the immiscible (with water) organic solvent. Therefore,

$$\left(C_{I_2}\right)_w = \left(C_{I_2}\right)_o / K_d$$

If C is the total concentration of KI, that is I^- initially present, and C_w is the total concentration of iodine (that is, free $I_2 + I_3^-$) in the aqueous layer at equilibrium, then,

$$\left(C_{I_3^-}\right)_w = C_w - \left(C_{I_2}\right)_w = C_w - \left(C_{I_2}\right)_o / K_d$$

$$C = (C_{I^-})_w + \left(C_{I_3^-}\right)_w$$

$$\therefore (C_{I^-})_w = C - \left(C_{I_3^-}\right)_w = C - \left[C_w - \left(C_{I_2}\right)_o / K_d\right]$$

Therefore, the working expression for the equilibrium constant becomes

$$K = \frac{\left[C_w - \left(C_{I_2}\right)_o / K_d\right]}{\left[C - \left(C_w - \left(C_{I_2}\right)_o / K_d\right)\right]\left[\left(C_{I_2}\right)_o / K_d\right]}$$

Procedure: *(Please do not report in your laboratory notebook)*

1. Prepare 250 ml of standard (N/20) $K_2Cr_2O_7$ solution and 250 ml of standard (N/20) KI solution by accurate weighing.

2. Prepare 500 ml approximately (N/20) sodium thiosulphate solution and standardize the same against the standard (N/20) $K_2Cr_2O_7$ solution iodometrically using starch indicator using the usual procedure.
3. Prepare four experimental sets of following compositions in 250 ml stoppered glass bottles:

Set	**I**	**II**	**III**	**IV**
Volume of KI solution (ml)	10	20	30	40
Volume of I_2 solution in organic solvent (ml)	40	40	40	40
Volume of water (ml)	90	80	70	60

4. Stopper the glass bottles properly and shake the mixtures thoroughly for 45 minutes and allow to settle till a clear separation of the two phases occurs.
5. Use the supplied partition coefficient value for the rest of the experiment.
6. For titration of I_2 in the organic layer take an aliquot of 10 ml, add 40 ml (two test tubes full) of water, and 1 g of KI. Shake thoroughly and titrate with the standard sodium thiosulphate solution of order (N/20) using starch indicator. Estimate the concentration iodine in organic layer and find $\left(C_{I_2}\right)_o$.
7. For titration of I_2 in the aqueous layer take an aliquot of 10 ml, add 40 ml (two test tubes full) of water. Shake thoroughly and titrate with the standard sodium thiosulphate solution of order (N/20) using starch indicator. Estimate the concentration iodine in aqueous layer and find C_w.
8. Calculate the value of K at room temperature, using the value of the partition coefficient, K_d, and interpret the results.

Results and Calculations:

1. Temperature of the experiment: … ℃
2. Supplied value of the partition coefficient (at … ℃): …
3. Weight of $\mathrm{K_2Cr_2O_7}$ taken: … gm. So, the strength of 250 ml of the $\mathrm{K_2Cr_2O_7}$ solution: … (N/10)
4. Standardization of the supplied $\mathrm{Na_2S_2O_3}$ solution:

No. of Obs.	Vol. of $K_2Cr_2O_7$	Burette reading for thiosulphate (ml)				Strength of sodium thiosulphate solution
		Initial	Final	Vol. reqd.	Mean	
1	10.0	0.0				(N/10)
2	10.0	0.0				
3	10.0	0.0				

5. Weight of KI taken: … gm. So, the strength of 250 ml of the KI solution: … (N/10)
6. Preparation of sets:

Set No.	Vol. of satd. Iodine soln. (ml)	Vol. of KI soln. (ml)	Vol. of CCl_4 (ml)	Total vol. (ml)
1	20	25	5	50
2	20	20	10	50

7. Titration of the aqueous and organic layers from the two sets:
   Volume of aqueous layer pipetted out (ml): 10.0 ml
   Volume of organic layer pipetted out (ml): 5.0 ml

Set No. (Layer)	No. of Obs.	Burette reading for thiosulphate (ml)				Concentration of molecular iodine in different layers
		Initial	Final	Vol. reqd.	Mean	
1 (Aqueous)	1	0.0				(N/10)
	2	0.0				(M)
1 (Organic)	1	0.0				(N/10)
	2	0.0				(M)
2 (Aqueous)	1	0.0				(N/10)
	2	0.0				(M)
	1	0.0				(N/10)

2 (Organic)	2	0.0				(M)	

8. Calculation of the equilibrium constant:

Set No.	$[I_2](aq)$	$[I_2](org)$	$[I_2^{free}](aq)$	$[I_3^-]$	$[KI^{initial}]$	$[KI^{equilibrium}]$	K	Mean K
1								
2								

Conclusion:

The equilibrium constant for the reaction $\mathrm{KI} + \mathrm{I_2} \rightleftharpoons \mathrm{KI_3}$ is found to be … at … ℃.

Experiment 5: To study the kinetics of saponification of ester by conductometric method.

Theory: When an ester ($\mathrm{R^1COOR^2}$), derived from a monocarboxylic acid ($\mathrm{R^1COOH}$) and a monohydric alcohol ($\mathrm{R^2OH}$), is treated with caustic alkali (NaOH), the ester is hydrolyzed to produce the alcohol and the sodium salt of the acid:

$$\mathrm{R^1COOR^2 + NaOH \rightarrow R^1COO^-Na^+ + R^2OH}$$

Or,

$$\mathrm{R^1COOR^2 + OH^- \rightarrow R^1COO^- + R^2OH}$$

Such an alkaline hydrolysis of an ester is called saponification.

Methyl acetate ($\mathrm{CH_3COOCH_3}$) on alkaline hydrolysis produces methanol ($\mathrm{CH_3OH}$) and acetate ($\mathrm{CH_3COO^-}$):

	$\mathrm{CH_3COOCH_3}$	+ $\mathrm{OH^-}$	→ $\mathrm{CH_3COO^-}$	+ $\mathrm{CH_3OH}$
$t = 0$	a	a	0	0
$t = t$	$a - x$	$a - x$	x	x
$t = \infty$	0	0	a	a

The overall reaction is kinetically of second order, being first order with respect to each of the reactants, the ester and the hydroxyl ions. The rate of the overall reaction may be expressed as:

$$\mathrm{Rate} = -\frac{d[\mathrm{ester}]}{dt} = k[\mathrm{ester}][\mathrm{OH^-}]$$

where k is the rate constant in L $\mathrm{mol^{-1}}$, and $[\cdots]$ stands for the concentration in mol $\mathrm{L^{-1}}$. If the initial concentrations of both the ester and the alkali be a mol $\mathrm{L^{-1}}$ and those after time t be $(a - x)$, where, x is the amount of alkali/ester consumed, then,

$$\frac{dx}{dt} = k(a - x)^2$$

Integration of the above equation, for the condition that at $t = 0$, $x = 0$ leads to

$$k = \frac{1}{at}\frac{x}{a - x}$$

The progress of the reaction can be monitored by measuring the electrolytic conductance of the reaction mixture, since the highly conducting OH^- ions ($\lambda_0 = 198.5$ $\mathrm{ohm^{-1}\ cm^2\ equiv^{-1}}$) are replaced by weakly conducting CH_3COO^- ions ($\lambda_0 = 40.9$ $\mathrm{ohm^{-1}\ cm^2\ equiv^{-1}}$). If C_0, C_t and C_∞ be the conductance values of the reaction mixture at the times $t = 0, t$ and at the completion of the reaction ($t = \infty$), then,

$$a \propto (C_0 - C_\infty), \qquad x \propto (C_0 - C_t), \qquad (a - x) \propto (C_t - C_\infty)$$

Therefore,

$$\frac{(C_0 - C_t)}{(C_t - C_\infty)} = kat$$

A plot of $(C_0 - C_t)/(C_t - C_\infty)$ versus t will be a straight line passing through the origin with a positive slope of ka. Thus, k may be evaluated from the relation, $k = \mathrm{slope}/a$.

Procedure: *(Please do not report in your laboratory notebook)*

1. Record the room temperature.
2. Prepare 100 ml of standard (N/10) oxalic acid solution by accurate weighing.
3. Standardize the supplied approximately (N/10) NaOH solution using the standard oxalic acid.
4. Standardize the supplied approximately (N/10) AcOH solution using the standardized NaOH.
5. Quantitatively dilute the standardized NaOH solution to exactly (N/60).
6. Quantitatively dilute the standardized AcOH solution to exactly (N/60).
7. Measure the conductance of the exactly (N/120) NaOAc solution [25 ml of (N/60) NaOH solution + 25 ml of (N/60) acetic acid solution].
8. Start the reaction by mixing 25 ml of the supplied exact (N/60) solution of the ester (methyl acetate) and 25 ml of (N/60) NaOH solution, and record the kinetic data.
9. Plot a graph of $(C_0 - C_t)/(C_t - C_\infty)$ against t and calculate the rate constant.

Results and Calculations:

1. Experimental temperature:

Temperature before expt. (°C)	Temperature after expt. (°C)	Mean temperature (°C)

2. Preparation of 100 ml standard (N/10) oxalic acid solution: …… gm of oxalic acid was accurately weighed in an electronic balance and was subsequently dissolved in 100 ml distilled water to prepare a …… (N) oxalic acid solution.
3. Standardization of the supplied approximately (N/10) NaOH solution: Volume of oxalic acid solution pipetted out = 25 ml

No. of Obs.	Burette reading		Volume of NaOH required (ml)	Mean volume of NaOH required (ml)	Strength of NaOH
	Initial	Final			
1.					
2.					
3.					

4. Standardization of the supplied approximately (N/10) acetic acid solution using the standardized NaOH solution: Volume of the supplied approximately (N/10) acetic acid solution pipetted out = 25 ml

No. of Obs.	Burette reading		Volume of NaOH required (ml)	Mean volume of NaOH required (ml)	Strength of the unknown acid
	Initial	Final			
1.					
2.					
3.					

5. …… ml of the …… (N) solution of NaOH was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water to prepare an exact (N/60) solution.
6. 25 ml of the (N/60) NaOH solution and 25 ml of conductivity was mixed in a 100 ml beaker, and its conductance (C_0) was measured to be …… mS.
7. …… ml of the … … (N/10) solution of acetic acid was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water to prepare an exact (N/60) solution.
8. Conductance of (N/120) solution of sodium acetate [25 ml of (N/60) NaOH solution + 25 ml of (N/60) acetic acid solution], $(C_\infty) =$ …… mS.
9. Supplied an exact (N/60) solution of the ester (methyl acetate).

10. Kinetic data

No.	Time (min:sec)	C_t (mS)	No.	Time (min:sec)	C_t (mS)
1.			11.		
2.			12.		
3.			13.		
4.			14.		
5.			15.		
6.			16.		
7.			17.		
8.			18.		
9.			19.		
10.			20.		

From the graph of $(C_0 - C_t)/(C_t - C_\infty)$ against t:
Rate constant, $k = \text{slope}/a, = \ldots\ldots L\ \text{mol}^{-1}$, where $a = 1/120\ \text{mol L}^{-1}$.

Conclusion: The rate constant, k for the saponification reaction is found to be …… L mol^{-1} at …… °C.

Experiment 6: To determine the ionization/dissociation constant of weak monobasic acid by conductometric method.

Theory: A weak monobasic acid, HA, is partially ionized in an aqueous solution. The degree of ionization, α, at any temperature increases with dilution.

$$HA + \text{water} \rightleftharpoons H^+(aq) + A^-(aq)$$
$$c(1-\alpha) \qquad\qquad c\alpha \qquad\quad c\alpha$$

The degree of ionization, α, at a particular concentration c of the weak electrolyte HA may be well approximated by the ratio, Λ/Λ_0, where Λ is the equivalent conductance of HA at the concentration c and Λ_0 is its equivalent conductance at infinite dilution. The ionization constant (K_a) of the weak acid HA may be defined as

$$K_a = \frac{a_{H^+}a_{A^-}}{a_{HA}} = \frac{[H^+][A^-]}{[HA]} \cdot \frac{f_{H^+}f_{A^-}}{f_{HA}} \cong \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

This is so, because the activities, a's, of the different species may be replaced by $a = fc$, where f is the ionic activity coefficient and c is the molar concentration. The terms $[\cdots]$ are the concentration terms c in g-mole/lit or g-ion/lit. For a dilute solution of a weak acid, the ionic strength of the medium will be very low, and the numerical value of the activity coefficients, f's, are very close to unity (by the Debye-Hückel limiting law). Now, substituting $\alpha = \Lambda/\Lambda_0$, one obtains

$$K_a = \frac{c(\Lambda/\Lambda_0)^2}{1 - \Lambda/\Lambda_0}$$

The above equation on rearrangement yields

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \left(\frac{1}{K_a\Lambda_0^2}\right)\Lambda c$$

If a series of solutions of the weak acid HA of different concentrations are prepared and their equivalent conductance values are determined by measuring their specific conductance values in a cell of known cell constant, then by plotting $\frac{1}{\Lambda}$ (along y axis) against Λc (along x axis), one may obtain a straight line with a positive intercept of $\frac{1}{\Lambda_0}$ and a positive slope of $\frac{1}{K_a\Lambda_0^2}$. Thus, K_a may be calculated using the relation

$$K_a = \frac{(\text{intercept})^2}{\text{slope}},$$

provided Λ_0 is determined with sufficient accuracy. Therefore, by this method, the ionization constant K_a and as well as the equivalent conductance at infinite dilution, Λ_0 of a weak electrolyte HA can be determined.

Procedure:

1. Prepare 250 ml of a standard KCl solution (strength slightly higher than N/10) in conductivity water. Prepare 100 ml of an exact (N/10) KCl solution by accurate weighing and 100 ml of an exact (N/100) KCl solution by quantitatively diluting the prepared standard (N/10) KCl solution with conductivity water.
2. Rinse a 100 ml beaker and the conductivity cell with the exact (N/100) KCl solution thoroughly and then pour sufficient volume of this solution into the beaker so that the electrodes of the cell are completely immersed in the solution. Record the conductance. Repeat this procedure with the exact (N/10) KCl solution. Calculate the mean cell constant from the measured conductance values of these two solutions, using the literature values of the specific conductance of KCl solutions at these concentrations at the same temperature.
3. Prepare 100 ml of standard (N/2) acetic acid solution. Titrate it for standardization. Prepare 100 ml an exact (N/50) acetic acid solution by accurate dilution of the standard (N/2) solution with conductivity water.
4. In a clean, dry 100 ml beaker take 50 ml of (N/50) acetic acid solution using a 25 ml pipette. Dip the clean, dry conductivity cell into this solution, stir well and record the conductance. Carefully pipette out 25 ml of (N/50) acetic acid solution and pour in exactly 25 ml conductivity water into the cell using the same pipette after washing it properly. Mix the solution well and record the conductance of this (N/100) acetic acid solution as before. Follow the same procedure to obtain (N/200), (N/400), and (N/800) acetic acid solutions and record their conductance values following the same procedure.
5. Calculate the equivalent conductance values of all the acetic acid solutions using the mean value of the cell constant with the aid of the relation $\Lambda = 1000L_s/C$.
6. Plot $1/\Lambda$ versus Λc and find Λ_0 from the intercept, and then K_a from the slope and intercept using the equation

$$K_a = \frac{(\text{intercept})^2}{\text{slope}}$$

Results and Calculations:

1. Experimental temperature:

Temperature before expt. (°C)	Temperature after expt. (°C)	Mean temperature (°C)

2. Preparation of 100 ml standard (N/10) oxalic acid solution: ……gm of oxalic acid was accurately weighed in an electronic balance and was subsequently dissolved in 100 ml distilled water to prepare a …… (N) oxalic acid solution.
3. Standardization of thesupplied approximately (N/10) NaOH solution:Volume of oxalic acid solution pipetted out = 10 ml

No. of Obs.	Burette reading		Volume of NaOH required (ml)	Mean volume of NaOH required (ml)	Strength of NaOH
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

4. Standardization of the supplied approximately (N/50) unknown acid solution using the standardized NaOH solution: Volume of the supplied approximately (N/50) unknown acidsolution pipetted out = 25 ml

	Burette reading			

No. of Obs.	Initial	Final	Volume of NaOH required (ml)	Mean volume of NaOH required (ml)	Strength of the unknown acid
1.	0.0				
2.	0.0				
3.	0.0				

5. …….. ml of the x(N/50) solution of the unknown acid was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with conductivity water to prepare an exact (N/50) solution.
6. Preparation of exact 100 ml (N/10) KCl solution: …… gm of KCl was accurately weighed in an electronic balance and was subsequently dissolved in 100 ml distilled water to prepare anexact (N/10) KCl solution.
7. 10 ml of the exact (N/10) KCl solution was transferred using a 10 ml pipette into a 100 ml volumetric flask and the volume was made up to the mark with distilled water to prepare an exact 100 ml (N/100) KCl solution.
8. Determination of cell constant:

Solution used	Conductance (ohm^{-1})	Specific conductance ($ohm^{-1}cm^{-1}$) [Reported at experimental temperature]	Cell constant (cm^{-1})
(N/10) KCl			
(N/100) KCl			

The average cell constant: …… cm^{-1}.

9. Conductance of the supplied conductivity water = …… S at ……℃.
10. Recording conductance values and calculation of equivalent conductance values:

c	Conductance (μS)	Corrected Conductance (μS)	Specific conductance ($\mu S cm^{-1}$)	Equivalent conductance, Λ	Λc	$1/\Lambda$
(N/50)						
(N/100)						
(N/200)						
(N/400)						
(N/600)						
(N/800)						

11. From the graph,
    (a) Intercept = ……,$\Lambda_0 = \cdots$
    (b) Slope = ……,

$$K_a = \frac{(\text{intercept})^2}{\text{slope}} = \cdots$$

Also calculate the value of K_a using the theoretical value of Λ_0 (use the temperature corrected values, if possible).

Conclusion: The $K_a$of the supplied unknown acid is found to be …… at …… °C.

SEMESTER – IV

(UNDER THE CBCS PATTERN)

Experiment 1: To determine the solubility product of a sparingly soluble salt (in water and/or in an electrolyte solution with/without common ions) by titrimetric method.

Theory: The solubility of a solute in a solvent at a particular temperature is defined as the number of grams of the solute required to saturate 100 grams of the solvent to produce a saturated solution that remains in equilibrium with the undissolved solute. If S_0 be the solubility, then the concentration of the saturated solution is $10S_0/M$ molal, where M is the molar mass of the solute. The saturated

solution of sparingly soluble salts is sufficiently dilute, as such the concentrations in molarity are very close to molality. For such solutions, therefore, the molar concentrations may be conveniently used as the measure of their solubility. The solubility product of a sparingly soluble electrolyte is the product of the activities of the ions (raised to proper power), remaining in equilibrium with the solid solute in a saturated solution at a particular temperature. Solubility equilibria of a 1:1 sparingly soluble salt, A^+B^-, in aqueous media may be represented according to:

$$A^+B^-(solid) \rightleftharpoons A^+B^-(aq) \rightleftharpoons A^+(aq) + B^-(aq)$$

for which the activity solubility product (K_a) and the concentration solubility product (K_c) are defined as

$$K_a = a_{A^+}(aq) \times a_{B^-}(aq)$$
$$K_c = [A^+(aq)] \times [B^-(aq)]$$

where a's represents the activities and [ ]'s are the molar concentrations. Since, activity, a is concentration, [ ] times the activity coefficient, f, $a_{A^+} = [A^+]f_{A^+}$ and $a_{B^-} = [B^-]f_{B^-}$

$$\therefore K_a = K_c(f_{A^+}f_{B^-}) = K_c f_{\pm}^2$$

where, $f_{\pm}$ is the mean ionic activity coefficient of the electrolyte. The solubility product is an equilibrium constant at a constant temperature, since the activity of the pure solute is unity. As the saturated solution of a sparingly soluble salt is very dilute, the activity of the ions become numerically equal to their molar concentrations, since the mean ionic activity coefficient, $f_{\pm}$, tends to be unity.

$$\therefore K_a = K_c = S_0 \times S_0 = S_0^2$$

where S_0 is the solubility of the salt A^+B^- in moles per litre. Potassium hydrogen tartrate (KHTa) is a sparingly soluble salt, which ionizes in aqueous solution as

$$KHTa(s) \rightleftharpoons K^+(aq) + HTa^-(aq)$$

If the concentration of the HTa^- ion in the saturated solution of KHTa in water at room temperature is S moles/litre, then the concentration solubility product, K_c, may be obtained from the relation $K_c = S^2$. The solubility, S' of the salt (KHTa) in a solution containing a common ion (for example, KCl), is lower than that in pure water. Since the solubility product K_c is a constant,

$$K_c = (S' + C)S'$$

where, C is the concentration of the external electrolyte (say KCl). In the presence of an electrolyte, having no ions in common (for example, $NaNO_3$), the ionic strength of the medium increases, and the mean ionic activity coefficient decreases (a consequence of the Debye-Hückel limiting law), and there is a consequent increase in the solubility (S) of the sparingly soluble salt. As a result, K_c increases, but K_a remains unaltered at a particular temperature.

Procedure:

1. Prepare 100 ml of standard oxalic acid solution of order (N/10).
2. Standardize the supplied approximately (N/10) NaOH solution using the standard oxalic acid.
3. In two clean and dry 250 ml stoppered bottles take 2 gm each of the supplied sparingly soluble salt (we will use potassium hydrogen tartrate, abbreviated as KHTa). In one bottle add approximately 100 ml of distilled water and in another bottle add 100 ml of the supplied electrolyte solution. Shake the bottles until (~40 minutes) the equilibrium is reached and a saturated solution is obtained. Check that some solid remains undissolved. If necessary, add some more of the sparingly soluble salt and shake. Allow it to settle for 10 minutes.
4. Dry filter the solution and reject first few drops of the filtrate). Collect the residual filtrate in two separate clean and dry 100 ml conical flasks. Take 10 ml of the filtrates (separately) as aliquots and titrate against the standardized NaOH solution using phenolphthalein as indicator. Perform each titration twice.
5. Determine the solubility and the solubility product of the supplied salt in water and also in the supplied electrolyte solution.
6. Draw your conclusion appropriately.

Results and Calculations:

1. Temperature of the experiment: ____ ℃

2. Preparation of standard oxalic acid solution of order (N/10):
   Weight of oxalic acid taken = _____ gm
   Strength of oxalic acid solution: _____ (N/10) = _____ (N)
3. Standardization of the supplied approximately (N/10) NaOH solution:
   Volume of oxalic acid solution pipetted out = 10 ml

No. of Obs.	Burette reading		Vol. of NaOH required (ml)	Mean vol. of NaOH required (ml)	Strength of NaOH
	Initial	Final			
1					
2					
3					

   The standard NaOH solution was quantitatively diluted to ____ (N/20): Exactly 50 ml of ____ (N/10) NaOH solution was in a 100 ml volumetric flask using and burette, and the volume was made up to the mark with distilled water to prepare _____ (N/20) NaOH solution.
4. Composition of sets:

Set	Amount of KHTa (gm)	Vol. of water/electrolyte (ml)
Set-1		100 (water)
Set-2		100 (electrolyte)

5. Titration of Set-1:
   Volume of the filtrate (from Set-1) taken = _____ ml

No. of Obs.	Burette reading		Vol. of NaOH required (ml)	Mean vol. of NaOH required (ml)	Strength of the filtrate in Set-1
	Initial	Final			
1					
2					$S =$
3					

6. Titration of Set-2:
   Volume of the filtrate (from Set-2) taken = _____ ml

No. of Obs.	Burette reading		Vol. of NaOH required (ml)	Mean vol. of NaOH required (ml)	Strength of the filtrate in Set-2
	Initial	Final			
1					
2					$S' =$
3					

7. Strength of the supplied electrolyte (KCl) solution: $C = 0.01$ (N)
8. Calculation of the concentration solubility product at _____ °C:
   (a) From Set-1: $K_c = S^2 =$ _____ moles^2/litre^2
   (b) From Set-2: $K_c = (S' + C)S' =$_____ moles^2/litre^2

Conclusion:

Experiment 2: To potentiometrically estimate of the strength of a supplied unknown Mohr's salt solution with a standard solution of $\mathbf{K_2Cr_2O_7}$.

Theory: When the $Fe^{3+}|Fe^{2+}$ redox system is coupled with a saturated calomel electrode (SCE), $Pt(s)|Hg(l)|Hg_2Cl_2(s)|KCl(aq), saturated|$, as the reference electrode, the following electrochemical cell is produced:

$$\underset{(-)}{Pt(s)|Hg(l)|Hg_2Cl_2(s)|KCl(aq), saturated|agar - KCl(saturated)|}\underset{(+)}{Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s)}$$

The KCl (saturated) salt-bridge is used to eliminate the liquid junction potential. The half-cell reactions at the electrodes are

$$\text{LHE: } 2Hg(l) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$
$$\text{RHE: } Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$

The overall reaction is

$$2Hg(l) + 2Cl^-(aq) + 2Fe^{3+}(aq) \rightleftharpoons Hg_2Cl_2(s) + 2Fe^{2+}(aq)$$

The EMF of the cell, E_{cell}, is given by

$$E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}} = E_{Fe^{3+}|Fe^{2+}} - E_{\text{SCE}}$$
$$= E^0_{Fe^{3+}|Fe^{2+}} + 0.059\log([Fe^{3+}]/[Fe^{2+}]) - E_{\text{SCE}} \text{ (at 25°C)}$$

Since E_{SCE} remains unaltered if the temperature remains unchanged, the EMF of the cell (E_{cell}) varies with the variation of the ratio $[Fe^{3+}]/[Fe^{2+}]$. If an oxidant, say $K_2Cr_2O_7$, is added to a solution of Fe^{2+} in the acid medium, the concentration of Fe^{2+} will fall and that of Fe^{3+} will rise due to the reaction:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) = 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O.$$

With the progressive addition of the oxidant the ratio,$[Fe^{3+}]/[Fe^{2+}]$, increases progressively, resulting in an increase in the value of E_{cell}. At the half-equivalence point, exactly half of the Fe^{2+} originally present is converted to Fe^{3+}, and the ratio $[Fe^{3+}]/[Fe^{2+}]$ becomes unity. At this point,

$$E_{\text{cell}} = E_{1/2} = E^0_{Fe^{3+}|Fe^{2+}} - E_{\text{SCE}}$$
$$\therefore\ E^0_{Fe^{3+}|Fe^{2+}} = E_{1/2} + E_{\text{SCE}}$$

E_{SCE} is obtainable from the literature. Thus $E^0_{Fe^{3+}|Fe^{2+}}$ at the room temperature may be obtained if $E_{1/2}$ is determined. Near the equivalence point the ratio$[Fe^{3+}]/[Fe^{2+}]$ increases abruptly on addition of even a very small amount of the oxidant (titrant), leading to a sharp jump in the value of E_{cell}. After the equivalence point is crossed, the $Fe^{3+}|Fe^{2+}$ redox system at the RHE is replaced by the $Cr_2O_7^{2-}, H^+|2Cr^{3+}$ couple. Further addition of the oxidant to the system produces only a small change in the value of E_{cell}. A potentiometric titration curve may be obtained by plotting E_{cell} versus the number of drops of the standard $K_2Cr_2O_7$ solution. From the smooth (sigmoid) curve, the number of drops of the standard $K_2Cr_2O_7$ solution required to completely oxidize Fe^{2+} to Fe^{3+}may be determined. Hence the number of drops (n) of the standard $K_2Cr_2O_7$ solution required to oxidize just the half of the Fe^{2+} originally present may be calculated and the corresponding value of $E_{\text{cell}} = E_{1/2}$may be found out from the graph. Alternatively, the amount of $K_2Cr_2O_7$ solution corresponding to the equivalence point may be obtained from the maximum of the absolute derivative, $|\Delta E_{\text{cell}}/\Delta n|$ plot against n. The volume of the standard $K_2Cr_2O_7$ solution corresponding to n drops can be determined from the drop calibration. Using the relation $V_1S_1 = V_2S_2$ is used to determine the unknown strength of the supplied Mohr's salt solution. The value of $E^0_{Fe^{3+}|Fe^{2+}}$ at the experimental temperature is determined using the literature value of E_{SCE} and the graphically obtained $E_{1/2}$ value.

Procedure:

1. (a) Prepare 50 ml of a standard (N/2) solution of $K_2Cr_2O_7$ by accurate weighing.
   (b) ~~Prepare 50 ml of ~ (N/10) solution of Mohr's salt in ~ 2(N) H_2SO_4 solution.~~ (Supplied)
2. Take an aliquot of 10 ml of Mohr's salt solution in a beaker and dip a clean Pt electrode into this solution. Add sufficient volume of approximately 2(N) H_2SO_4 solution so that the electrodes dip in

properly. Connect this half-cell with a saturated calomel electrode (SCE) through an agar-KCl (saturated) salt bridge. Complete the connections of this experimental cell with the potentiometer.

3. Standardize the potentiometer with a standard cell.
4. Determine the number of drops of standard (N/2) solution of $K_2Cr_2O_7$ that constitute 1.0 ml (drop calibration).
5. Measure the EMF of the experimental cell.
6. Add 2-3 drops of the standard (N/2) solution of $K_2Cr_2O_7$, stir gently with a glass rod and record the EMF. Repeat this procedure till the equivalence point is reached, which is indicated by a sharp increase in the EMF. Take a few more readings beyond the equivalence point.
7. Plot (a) EMF versus the mean number of drops of $K_2Cr_2O_7$ solution, (b) derivative of EMF with respect to the mean number of drops of $K_2Cr_2O_7$ solution versus the mean number of drops of $K_2Cr_2O_7$ solution, hence the value of EMF corresponding to the half-neutralization point accordingly and calculate the formal potential of the Fe^{3+}/Fe^{2+} system using the literature value of the electrode potential of the SCE (with proper temperature correction).

Results and Calculations:

1. Temperature of the experiment: … °C
2. Preparation of standard $K_2Cr_2O_7$ solution of order $(N/2)$.
   Weight of $K_2Cr_2O_7$ taken = … gm.
   ∴ The strength of $K_2Cr_2O_7$ solution = $(\ldots/2.45)(N/2)$ = … (N)
3. Drop calibration for $S(N/2)$ $K_2Cr_2O_7$ solution.
   1 ml of $0.501(N)$ $K_2Cr_2O_7$ solution ≡ ⋯ drops.
   ∴ Volume of one drop of $S(N/2)$ $K_2Cr_2O_7$ solution $= 1/\ldots = \cdots$ ml.
4. Potentiometric titration of the supplied Mohr's salt solution of order $(N/10)$ using the … (N) $K_2Cr_2O_7$ solution.

No. of drops	Total no. of drops (n)	Volume (ml)	Measured EMF (V)	$d(EMF)/dV$

5. Graphical representation of the experimental data:
6. Calculation of the strength of the supplied Mohr's salt solution:
   No. of drops needed for equivalence $=$ … drops (from the graph of d(EMF)/dn vs. n for known $K_2Cr_2O_7$)
   ∴ Volume needed for equivalence $= \cdots \times \ldots = \cdots$ ml
   ∴ The strength of the supplied Mohr's salt solution $= \cdots (N)$

Conclusion:

Experiment 3: Potentiometric determination of the concentration of a supplied $\sim(N/100)\mathbf{AgNO_3}$ solution, and the solubility product of $\mathbf{AgCl}$.

Theory: When the $Ag^+|Ag(s)$ redox electrode is coupled with a saturated calomel electrode (SCE), $Pt(s)|Hg(l)|Hg_2Cl_2(s)|KCl(aq), saturated|$, as the reference electrode, the following electrochemical cell is produced:

$$\underset{(-)}{Pt(s)|Hg(l)|Hg_2Cl_2(s)|KCl(aq), saturated|agar - KCl(saturated)|}\underset{(+)}{Ag^+(aq)|Ag(s)}$$

The KCl (saturated) salt-bridge is used to eliminate the liquid junction potential. The half-cell reactions at the electrodes are

$$\text{LHE: } 2Hg(l) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$
$$\text{RHE: } Ag^+(aq) + e^- \rightleftharpoons Ag(s)$$

The overall reaction is

$$2Hg(l) + 2Cl^-(aq) + 2Ag^+(aq) \rightleftharpoons Hg_2Cl_2(s) + 2Ag(s)$$

The EMF of the cell, E_{cell}, is given by

$$E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}} = E_{Ag^+|Ag(s)} - E_{\text{SCE}} = E^0_{Ag^+|Ag(s)} + 0.059\log\left(a_{Ag^+}/a_{Ag(s)}\right) - E_{\text{SCE}} \text{ (at 25°C)}$$

$Ag(s)$ being in the standard state, its activity will be unity. For a dilute solution, the activity (a) of $Ag^+(aq)$ may be replaced by the numerical value of its concentration, $[Ag^+]$. Thus,

$$E_{\text{cell}} = E^0_{Ag^+|Ag(s)} + 0.059\log[Ag^+] - E_{\text{SCE}}$$

Since $E^0_{Ag^+|Ag(s)}$ and E_{SCE} are fixed, E_{cell} depends on $[Ag^+]$. [The standard reduction potential of an electrode may be defined as the EMF of the cell produced by the coupling the standard hydrogen electrode on the left and the electrode under consideration on the right with all the reactants and products at unit activities.] As KCl solution is added to the $AgNO_3$ solution, the following reaction takes place

$$AgNO_3\,(aq) + KCl\,(aq) = KNO_3\,(aq) + AgCl\,(s)$$

AgCl being sparingly soluble, $[Ag^+]$ decreases as more and more KCl solution is added, resulting in the decrease of E_{cell} with the increase in the number of drops (n) of KCl solution. Near the equivalence point, addition of a small volume (1 drop) of KCl solution removes practically all the Ag^+ ions from the solution. This produces an abrupt decrease in E_{cell} and a large value of the $\Delta E_{\text{cell}}/\Delta n$ value. All the Ag^+ ions present in the solution at the equivalence point come from the dissociation of the sparingly soluble AgCl produced:

$$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
$$\therefore [Ag^+] = [Cl^-]$$

The activity solubility product, K_a, of AgCl may be defined as

$$K_a = a_{Ag^+}a_{Cl^-} = [Ag^+][Cl^-]f_{Ag^+}f_{Cl^-} = K_{sp}f_{\pm}^2$$

where K_{sp} is the concentration solubility product, or simply the solubility product, and $f_{\pm}$ is the mean ionic activity coefficient. For a dilute solution, the activities may be replaced by the numerical value of concentrations.

$$\therefore K_{sp} = [Ag^+][Cl^-]$$

Hence, at the equivalence point, $[Ag^+] = [Cl^-]$, so that $[Ag^+] = \left(K_{sp}\right)^{1/2}$. Substituting this value of $[Ag^+]$ in the last expression for E_{cell}, one obtains the EMF of the cell at the equivalence point

$$E_{\text{cell}}^{\text{equivalence}} = E^0_{Ag^+|Ag(s)} + \frac{0.059}{2}\log K_{sp} - E_{\text{SCE}}$$

Thus, by determining $E_{\text{cell}}^{\text{equivalence}}$ and knowing $E^0_{Ag^+|Ag(s)}$ from the literature and $E_{\text{SCE}} = 0.2415 - 7.6\times10^{-4}(t-25)$ V, one may calculate K_{sp} using the above relation. After the equivalence point the addition of more KCl solution will lower the concentration of Ag^+ further. The constancy of K_{sp} demands

$$[Ag^+] = K_{sp}/[Cl^-]$$

Hence, E_{cell} will decrease with increase of $[Cl^-]$ according to

$$E_{\text{cell}} = E^0_{\text{Ag}^+|\text{Ag(s)}} + 0.059 \log K_{sp} - 0.059 \log[\text{Cl}^-] - E_{\text{SCE}} = E^f_{\text{Ag}^+|\text{Ag(s)}} - E_{\text{SCE}} - 0.059 \log[\text{Cl}^-]$$

where $E^f_{\text{Ag}^+|\text{Ag(s)}}$ is the formal potential of $\text{AgCl (s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-\text{(aq)}$ redox system, and is given by

$$E^f_{\text{Ag}^+|\text{Ag(s)}} = E^0_{\text{Ag}^+|\text{Ag(s)}} + 0.059 \log K_{sp}$$

From the plot of E_{cell} versus the number of drops of KCl solution, it is possible to find the number of drops (n) of KCl required to completely precipitate the Ag^+ ions present in the solution, and the value of E_{cell} at the equivalence point. The derivative plot, $|\Delta E_{\text{cell}}/\Delta n|$ versus n shows a maximum at the value of n corresponding to the equivalence point. The strength of the AgNO_3 solution may be calculated using the relation $V(\text{AgNO}_3) \times S(\text{AgNO}_3) = V(\text{KCl}) \times S(\text{KCl})$. Thus, from the potentiometric titration, the strength of AgNO_3 solution may be determined. If a solution of KCl of unknown strength is provided, a similar potentiometric titration can be performed to determine its strength using the potentionmetrically standardized AgNO_3 solution.

Procedure:

1. Prepare 100 ml of a standard (N/10) KCl solution in distilled water by accurate weighing.
2. Pipette out 10 ml of the supplied approximately (N/100) AgNO_3 solution in a 100 ml beaker and dip the silver electrode in this solution. Add sufficient amount of distilled water so that the electrode dips properly. [This constitutes the experimental electrode $\text{Ag}^+|\text{Ag(s)}$.]
3. Set up the experimental cell by connecting the saturated calomel electrode (SCE) and the experimental electrode through the agar-KNO_3 salt-bridge.
4. Take the prepared KCl solution in a burette and determine the volume of 20 drops and then calculate the volume of 1 drop of KCl.
5. Connect the experimental cell with the standardized potentiometer.
6. Measure the EMF of the cell. Add 2 drops of standard (N/10) KCl solution, stir gently and record the E_{cell}. Repeat the procedure till 10 drops of the titrant are added. Then add 1 drop at a time, till the equivalence point is reached, which is indicated by a sharp decrease of E_{cell}. Take a few more readings beyond the equivalence point.
7. Plot (a) the observed E_{cell} values against the number of drops, n, of KCl solution added, (b) $|\Delta E_{cell}/\Delta n|$ versus n. Determine the equivalence point and the E_{cell} value at the equivalence point from the graph. Calculate the solubility product of AgCl using the literature value $E^0_{\text{Ag}^+|\text{Ag(s)}}$ and E_{SCE}.
8. Calculate the strength of the AgNO_3 solution by using the volume of standard KCl solution required at equivalence point (obtained graphically).

Results and Calculations:

1. Temperature of the experiment: … … °C
2. Preparation of standard KCl solution of order $(N/10)$.
   Weight of KCl taken = … … gm.
   ∴ The strength of KCl solution = $(\ldots \ldots/0.745)(N/10)$ = … … $(N/10)$
3. Drop calibration for … … $(N/10)$ KCl solution.
   1 ml of … … $(N/10)$ KCl solution = … … drops.
   ∴ Volume of one drop of … … $(N/10)$ KCl solution $= 1/\ldots \ldots$ = … … ml.
4. Potentiometric titration of the supplied AgNO_3 solution of order $(N/100)$ using the … … $(N/10)$ KCl solution.

No. of drops	Total no. of drops (n)	Volume (ml)	Measured EMF (V)	$\lvert d(EMF)/dV \rvert$
0				
2				
2				
2				

2				
2				
2				
2				
2				
2				
2				
2				
2				
2				
2				
2				
2				
2				

5. Calculations from the graph:
   Given, $E_{\mathrm{SCE}} = 0.2415 - 7.6 \times 10^{-4}(t - 25)$ V.

Conclusion:

Experiment 4: To determine the strength of an alkali solution and the pK_a value of a weak monobasic acid by pH-metric titration.

Theory: The pH of an aqueous solution can be measured using a glass-calomel electrode system in which the following electrochemical cell is formed:

$$\underset{(-)}{\mathrm{Pt(s)|Hg(l)|Hg_2Cl_2(s)|KCl(aq), saturated|agar - KCl(saturated)|glass - electrode}}\ \underset{(+)}{}$$

The left-hand electrode is the saturated calomel electrode (SCE) and the right-hand electrode is the glass electrode which is actually an ion-selective membrane electrode whose potential is reversible with respect to the H^+ ion concentration. The construction of the glass electrode is based on the observation that the electrical potential difference between a glass surface and an aqueous solution varies regularly with pH of the aqueous solution varies regularly with the pH of the aqueous solution except those which are very strongly acidic or very strongly alkaline. The electrode is made of a thin-walled bulb of low melting glass of high electrical conductivity. Inside the bulb is placed a solution of constant pH (a buffer solution, or, 1(N) HCl solution) together with a little quinhydrone and a platinum wire for electrical contact. The potential (E_g) of the glass electrode at 25 °C may be expressed according to,

$$E_g = E_g^0 + 0.059 \log a_{H^+} = E_g^0 - 0.059pH$$

For actual pH measurement, the glass electrode is standardized in buffer solutions of known pH values. Usually, potassium hydrogen phthalate (pH 4), phosphate (pH 7), and borax (pH 9.2), buffer solutions are used for calibration of the pH meter. The EMF (E_{cell}) the glass-calomel electrode cell is given by,

$$E_{cell} = E_g - E_{SCE} = E_g^0 - 0.059pH - E_{SCE}, \text{so that } pH = \left(E_g^0 - E_{SCE} - E_{cell}\right)/0.059$$

The pH value can be read off directly from the digital pH-meter calibrated with standard buffer solutions.

Ionization constant of a weak acid (HA) in aqueous solution may be represented according to $\mathrm{HA} \rightleftharpoons \mathrm{H^+ + A^-}$, of which the ionization constant (K_{H}) is given by the activity quotient of the ionization equilibrium,

$$K_a = \frac{a_{\mathrm{H}^+} \cdot a_{\mathrm{A}^-}}{a_{\mathrm{HA}}}$$

where, a's represents the activities of the respective species which are related to the molar concentration, c, according to $a = c \cdot f$, where f is the corresponding activity coefficient. In dilute aqueous solutions of weak acids, the ionic strength is very low, so the activity coefficients approach unity, hence, the concentrations approach activities. Consequently, the ionization constant (K_{H}) may be expressed as concentration quotients of the ionization equilibrium, according to

$$K_a = \frac{c_{\mathrm{H}^+} \cdot c_{\mathrm{A}^-}}{c_{\mathrm{HA}}}$$

When an amount (b mol.lit^{-1}) of a strong base (say NaOH) is added to the solution containing a known mount (c mol.lit^{-1}) of the weak acid (HA), so that, $b < c$, the acid is partly neutralized to form b amount of the salt, Na^+A^-, which remains completely ionized in the solution, that still contains $(c - b)$ amount of the HA

$$\underset{(c-b)}{\mathrm{HA}} + \underset{b}{\mathrm{Na^+OH^-}} \rightarrow \mathrm{Na^+} + \underset{b}{A^-} \quad \mathrm{H_2O}$$

Such a mixture of a weak acid (HA) with its salt (Na^+A^-) constitutes a buffer solution, which has the ability to resist the change of H^+ ion concentration when small amount of an acid or a base is added to it. Expressions for pH of such a buffer solution are the different forms of the Henderson equation which may be obtained by substituting the values of c_{A^-} (b) and c_{HA} $(c - b)$ in the expression for K_H, and transforming to logarithmic forms:

$$pH = pK_a + \log_{10}\frac{c_{\mathrm{A}^-}}{c_{\mathrm{HA}}} = pK_a + \log_{10}\frac{b}{c-b} = pK_a + \log_{10}\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]}$$

If the amount of base added is just half-equivalent of the acid present, that is, when $b = c/2$, then the above equations are transformed to, $pK_a = (pH)_{1/2}$, where, $(pH)_{1/2}$ means the pH of the solution at the half neutralization point. pK_a value of a weak acid is most conveniently determined by pH-metrically titrating a known amount of the acid in aqueous solution with a strong base of known strength. A pH-metric titration curve may be constructed by plotting the pH of the acid solution after each addition of the strong base and the equivalence point of the titration may be determined graphically. The pH of the solution corresponding to the half neutralization point may be read out from the pH titration curve. This is how the pK_a value can be determined.

Procedure:

1. Prepare 100 ml of a standard (N/10) oxalic acid solution by accurate weighing.
2. Standardize the supplied ~ (N/2) NaOH solution using the standard (N/10) oxalic acid solution.
3. Determine the number of drops per ml of the titrant [~ (N/2) NaOH] solution.
4. Pipette out 10 ml of the supplied solution of an unknown weak monobasic acid in a 100 ml beaker, add sufficient quantity of distilled water so that electrodes dip into it properly. Allow the system to attain equilibrium at the experimental temperature and record the pH.
5. Add 1-2 drops of the standardized (N/2) NaOH solution from a burette, mix uniformly and record the pH. Repeat the process until the end-point is reached (indicated by a sharp rise in the pH).
6. Plot (a) pH versus the total number of drops, n, of (N/2) NaOH solution, and (b) $\Delta pH/\Delta n$ versus the total number of drops, n, of (N/2) NaOH solution, and hence determine the value of pH corresponding to the half-neutralization point.
7. Determine the strength of the supplied solution of the unknown weak monobasic acid and its pK_a.

Results and Calculations:

1. Temperature of the experiment: _____ ℃
2. Preparation of standard oxalic acid solution of order (N/10): Weight of oxalic acid taken = _____ gm Strength of oxalic acid solution: _____ (N/10) = _____ (N)
3. Standardization of the supplied ~ (N/2) NaOH solution: Volume of oxalic acid solution pipetted out = 10 ml

No. of Obs.	Burette reading		Vol. of NaOH required (ml)	Mean vol. of NaOH required (ml)	Strength of NaOH
	Initial	Final			
1					
2					
3					

4. Drop calibration for … … $(N/2)\mathrm{NaOH}$ solution:

   1 ml of … … $(N/2)\mathrm{NaOH}$ solution = … … drops.

   ∴ Volume of one drop of … … $(N/2)\mathrm{NaOH}$ solution $= 1/\ldots\ldots =$ … … ml.

5. pH-metric titration of the supplied solution of the unknown weak monobasic acid using the … … $(N/2)\mathrm{NaOH}$ solution.

No. of drops	Total no. of drops, n	pH	$\Delta\mathrm{pH}/\Delta\mathrm{n}$	No. of drops	Total no. of drops, n	pH	$\Delta\mathrm{pH}/\Delta\mathrm{n}$

6. From the graphs:

Conclusion:

Experiment 5: To determine the strength of an alkali solution and the pK_{a_1} and pK_{a_2} values of a weak dibasic acid by pH-metric titration.

Theory: The pH of an aqueous solution can be measured using a glass-calomel electrode system in which the following electrochemical cell is formed:

$$\underset{(-)}{\mathrm{Pt(s)|Hg(l)|Hg_2Cl_2(s)|KCl(aq), saturated|agar-KCl(saturated)|glass-electrode}}\ \ \underset{(+)}{}$$

The left-hand electrode is the saturated calomel electrode (SCE) and the right-hand electrode is the glass electrode which is actually an ion-selective membrane electrode whose potential is reversible with respect to the H^+ ion concentration. The construction of the glass electrode is based on the observation that the electrical potential difference between a glass surface and an aqueous solution varies regularly with pH of the aqueous solution varies regularly with the pH of the aqueous solution except those which are very strongly acidic or very strongly alkaline. The electrode is made of a thin-walled bulb of low melting glass of high electrical conductivity. Inside the bulb is placed a solution of constant pH (a buffer solution, or, 1(N) HCl solution) together with a little quinhydrone and a platinum wire for electrical contact. The potential (E_g) of the glass electrode at 25 °C may be expressed according to,

$$E_g = E_g^0 + 0.059 \log a_{H^+} = E_g^0 - 0.059pH$$

For actual pH measurement, the glass electrode is standardized in buffer solutions of known pH values. Usually, potassium hydrogen phthalate (pH 4), phosphate (pH 7), and borax (pH 9.2), buffer solutions are used for calibration of the pH meter. The EMF (E_{cell}) the glass-calomel electrode cell is given by,

$$E_{cell} = E_g - E_{SCE} = E_g^0 - 0.059pH - E_{SCE}, \text{so that } pH = \left(E_g^0 - E_{SCE} - E_{cell}\right)/0.059$$

The pH value can be read off directly from the digital pH-meter calibrated with standard buffer solutions.

Ionization constant of a weak acid (HA) in aqueous solution may be represented according to $\mathrm{HA} \rightleftharpoons \mathrm{H^+ + A^-}$, of which the ionization constant (K_H) is given by the activity quotient of the ionization equilibrium,

$$K_a = \frac{a_{\mathrm{H^+}} \cdot a_{\mathrm{A^-}}}{a_{\mathrm{HA}}}$$

where, a's represents the activities of the respective species which are related to the molar concentration, c, according to $a = c \cdot f$, where f is the corresponding activity coefficient. In dilute aqueous solutions of weak acids, the ionic strength is very low, so the activity coefficients approach unity, hence, the concentrations approach activities. Consequently, the ionization constant (K_H) may be expressed as concentration quotients of the ionization equilibrium, according to

$$K_a = \frac{c_{\mathrm{H^+}} \cdot c_{\mathrm{A^-}}}{c_{\mathrm{HA}}}$$

When an amount (b mol.lit^{-1}) of a strong base (say NaOH) is added to the solution containing a known mount (c mol.lit^{-1}) of the weak acid (HA), so that, $b < c$, the acid is partly neutralized to form b amount of the salt, $\mathrm{Na^+A^-}$, which remains completely ionized in the solution, that still contains $(c - b)$ amount of the HA

$$\underset{(c-b)}{\mathrm{HA}} + \underset{b}{\mathrm{Na^+OH^-}} \rightarrow \mathrm{Na^+} + \underset{b}{A^-} \quad \mathrm{H_2O}$$

Such a mixture of a weak acid (HA) with its salt ($\mathrm{Na^+A^-}$) constitutes a buffer solution, which has the ability to resist the change of $\mathrm{H^+}$ ion concentration when small amount of an acid or a base is added to it. Expressions for pH of such a buffer solution are the different forms of the Henderson equation which may be obtained by substituting the values of $c_{\mathrm{A^-}}$ (b) and c_{HA} $(c - b)$ in the expression for K_H, and transforming to logarithmic forms:

$$pH = pK_a + \log_{10}\frac{c_{\mathrm{A^-}}}{c_{\mathrm{HA}}} = pK_a + \log_{10}\frac{b}{c-b} = pK_a + \log_{10}\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]}$$

If the amount of base added is just half-equivalent of the acid present, that is, when $b = c/2$, then the above equations are transformed to, $pK_a = (pH)_{1/2}$, where, $(pH)_{1/2}$ means the pH of the solution at the half neutralization point. pK_a value of a weak acid is most conveniently determined by pH-metrically titrating a known amount of the acid in aqueous solution with a strong base of known strength. A pH-metric titration curve may be constructed by plotting the pH of the acid solution after each addition of the strong base and the equivalence point of the titration may be determined graphically. The pH of the solution corresponding to the half neutralization point may be read out from the pH titration curve. This is how the pK_a value can be determined.

In case of a dibasic acid like the oxalic acid, the situation is slightly different owing to fact that there are two distinct dissociations, $\mathrm{H_2A} \rightleftharpoons \mathrm{H^+ + HA^-}$, followed by $\mathrm{HA^-} \rightleftharpoons \mathrm{H^+ + A^{2-}}$. The pK_{a_1} is obtained in the same way as for a monobasic acid, but in this case at least two half-equivalence points are present. One half-equivalence point occurs at one-half the volume of the first equivalence point, at which $pH = pK_{a_1}$. The second occurs at the volume that is at the midpoint between the first and second equivalence points, and at that point, $pH = pK_{a_2}$. Therefore, the pK_{a_2} essentially appears at the $3/4$th of the neutralization point of the total acid.

Procedure:

1. Prepare 100 ml of a standard (N/10) oxalic acid solution by accurate weighing.
2. Standardize the supplied ~ (N/2) NaOH solution using the standard (N/10) oxalic acid solution.
3. Determine the number of drops per ml of the titrant [~ (N/2) NaOH] solution.

4. Pipette out 10 ml of the supplied solution of an unknown weak dibasic acid in a 100 ml beaker, add sufficient quantity of distilled water so that electrodes dip into it properly. Allow the system to attain equilibrium at the experimental temperature and record the pH.
5. Add 1-2 drops of the standardized (N/2) NaOH solution from a burette, mix uniformly and record the pH. Repeat the process until the end-point is reached (indicated by a sharp rise in the pH).
6. Plot (a) pH versus the total number of drops, n, of (N/2) NaOH solution, and (b) $\Delta pH/\Delta n$ versus the total number of drops, n, of (N/2) NaOH solution, and hence determine the value of pH corresponding to the half-neutralization point.
7. Determine the strength of the supplied solution of the unknown weak dibasic acid and its pK_{a_1} and pK_{a_2} values.

Results and Calculations:

1. Temperature of the experiment: ____ ℃
2. Preparation of standard oxalic acid solution of order (N/10): Weight of oxalic acid taken = ____ gm
   Strength of oxalic acid solution: ____ (N/10) = ____ (N)
3. Standardization of the supplied ~ (N/2) NaOH solution: Volume of oxalic acid solution pipetted out = 10 ml

No. of Obs.	Burette reading		Vol. of NaOH required (ml)	Mean vol. of NaOH required (ml)	Strength of NaOH
	Initial	Final			
1					
2					
3					

4. Drop calibration for … … $(N/2)$NaOH solution:
   1 ml of … … $(N/2)$NaOH solution = … … drops.
   ∴ Volume of one drop of … … $(N/2)$NaOH solution $= 1/$… … = … … ml.
5. pH-metric titration of the supplied solution of the unknown weak dibasic acid using the … … $(N/2)$NaOH solution.

No. of drops	Total no. of drops, n	pH	ΔpH/Δn	No. of drops	Total no. of drops, n	pH	ΔpH/Δn

6. From the graphs:

Conclusion:

SEMESTER-V
(UNDER THE CBCS PATTERN)

INDEX

Date: ……

Basics of Numerical Analysis

Numerical analysis is the study of algorithms that use numerical approximation (as opposed to symbolic manipulations) for the problems of mathematical analysis (as distinguished from discrete mathematics). Numerical analysis naturally finds application in all fields of engineering and the physical sciences, but in the 21st century also the life sciences, social sciences, medicine, business and even the arts have adopted elements of scientific computations. The growth in computing power has revolutionized the use of realistic mathematical models in science and engineering, and subtle numerical analysis is required to implement these detailed models of the world. For example, ordinary differential equations appear in celestial mechanics (predicting the motions of planets, stars and galaxies); numerical linear algebra is important for data analysis; stochastic differential equations and Markov chains are essential in simulating living cells for medicine and biology.

Before the advent of modern computers, numerical methods often depended on hand interpolation formulas applied to data from large printed tables. Since the mid-20th century, computers calculate the required functions instead, but many of the same formulas nevertheless continue to be used as part of the software algorithms.

Numerical analysis continues the long tradition of seeking interpolation formulas, rather than exact symbolic answers, which can only be applied to real-world measurements by translation into digits, it gives approximate solutions within specified error bounds.

Direct and Iterative Methods in Numerical Analysis

Direct methods compute the solution to a problem in a finite number of steps. These methods would give the precise answer if they were performed in infinite precision arithmetic. Examples include Gaussian elimination, the QR factorization method for solving systems of linear equations, and the simplex method of linear programming. In practice, finite precision is used and the result is an approximation of the true solution (assuming stability).

In contrast to direct methods, iterative methods are not expected to terminate in a finite number of steps. Starting from an initial guess, iterative methods form successive approximations that converge to the exact solution only in the limit. A convergence test, often involving the residual, is specified in order to decide when a sufficiently accurate solution has (hopefully) been found. Even using infinite precision arithmetic these methods would not reach the solution within a finite number of steps (in general). Examples include Newton's method, the bisection method, and Jacobi iteration. In computational matrix algebra, iterative methods are generally needed for large problems.

Iterative methods are more common than direct methods in numerical analysis. Some methods are direct in principle but are usually used as though they were not, e.g. GMRES and the conjugate gradient method. For these methods the number of steps needed to obtain the exact solution is so large that an approximation is accepted in the same manner as for an iterative method.

Programming Languages in Numerical Analysis

A programming language is a formal language, which comprises a set of instructions that produce various kinds of output. Programming languages are used in computer programming to implement algorithms.

Most programming languages consist of instructions for computers. There are programmable machines that use a set of specific instructions, rather than general programming languages. Early ones preceded the invention of the digital computer, the first probably being the automatic flute player described in the 9th century by the brothers Musa in Baghdad, during the Islamic Golden Age. Since the early 1800s, programs have been used to direct the behaviour of machines such as Jacquard looms, music boxes and player pianos. The programs for these machines (such as a player piano's scrolls) did not produce different behaviour in response to different inputs or conditions. Thousands of different programming languages have been created, and more are being created every year. Many programming languages are written in an imperative form (i.e., as a sequence of operations to perform) while other languages use the declarative form (i.e. the desired result is specified, not how to achieve it).

The description of a programming language is usually split into the two components of syntax (form) and semantics (meaning). Some languages are defined by a specification document (for example, the C programming language is specified by an ISO Standard) while other languages (such as Perl) have a dominant implementation that is treated as a reference. Some languages have both, with the basic language defined by a standard and extensions taken from the dominant implementation being common. The term computer language is sometimes used interchangeably with programming language. However, the usage of both terms varies among authors, including the exact scope of each. One usage describes programming languages as a subset of computer languages. Similarly, languages used in computing that have a different goal than expressing computer programs are generically designated computer languages. For instance, mark-up languages are sometimes referred to as computer languages to emphasize that they are not meant to be used for programming.

All programming languages have some primitive building blocks for the description of data and the processes or transformations applied to them (like the addition of two numbers or the selection of an item from a collection). These primitives are defined by syntactic and semantic rules which describe their structure and meaning respectively. Programming languages share properties with natural languages related to their purpose as vehicles for communication, having a syntactic form separate from its semantics, and showing language families of related languages branching one from another. But as artificial constructs, they also differ in fundamental ways from languages that have evolved through usage. A significant difference is that a programming language can be fully described and studied in its entirety, since it has a precise and finite definition. By contrast, natural languages have changing meanings given by their users in different communities. While constructed languages are also artificial languages designed from the ground up with a specific purpose, they lack the precise and complete semantic definition that a programming language has.

In this course we have made use of the FORTRAN programming language for our purpose.

Date: ……

The FORTRAN Programming Language

FORTRAN (derived from Formula Translation) is a general-purpose, compiled imperative programming language that is especially suited to numeric computation and scientific computing. Originally developed by IBM in the 1950s for scientific and engineering applications, FORTRAN came to dominate this area of programming early on and has been in continuous use for over six decades in computationally intensive areas such as numerical weather prediction, finite element analysis, computational fluid dynamics, computational physics, crystallography and computational chemistry. It is a popular language for high-performance computing and is used for programs that benchmark and rank the world's fastest supercomputers.

FORTRAN encompasses a lineage of versions, each of which evolved to add extensions to the language while usually retaining compatibility with prior versions. Successive versions have added support for structured programming and processing of character-based data (FORTRAN 77), array programming, modular programming and generic programming (FORTRAN 90), high performance FORTRAN (FORTRAN 95), object-oriented programming (FORTRAN 2003), concurrent programming (FORTRAN 2008), and native parallel computing capabilities (Co-array FORTRAN 2008/2018).

FORTRAN's design was the basis for many other programming languages. Among the better known is BASIC, which is based on FORTRAN II with a number of syntax clean-ups, notably better logical structures, and other changes to work more easily in an interactive environment.

In late 1953, John W. Backus submitted a proposal to his superiors at IBM to develop a more practical alternative to assembly language for programming their IBM 704 mainframe computer. Backus' historic FORTRAN team consisted of programmers Richard Goldberg, Sheldon F. Best, Harlan Herrick, Peter Sheridan, Roy Nutt, Robert Nelson, Irving Ziller, Harold Stern, Lois Haibt, and David Sayre. Its concepts included easier entry of equations into a computer, an idea developed by J. Halcombe Laning and demonstrated in the Laning and Zierler system of 1952. Some of these programmers were chess players and were chosen to work at IBM with the thought being they had logical minds.

A draft specification for The IBM Mathematical Formula Translating System was completed by November 1954. The first manual for FORTRAN appeared in October 1956, with the first FORTRAN compiler delivered in April 1957. This was the first optimizing compiler, because customers were reluctant to use a high-level programming language unless its compiler could generate code with performance comparable to that of hand-coded assembly language.

The language was widely adopted by scientists for writing numerically intensive programs, which encouraged compiler writers to produce compilers that could generate faster and more efficient code. The inclusion of a complex number data type in the language made FORTRAN especially suited to technical applications such as electrical engineering.

By 1960, versions of FORTRAN were available for the IBM 709, 650, 1620, and 7090 computers. Significantly, the increasing popularity of FORTRAN spurred competing computer manufacturers to provide FORTRAN compilers for their machines, so that by 1963 over 40 FORTRAN compilers existed. For these reasons, FORTRAN is considered to be the first widely used cross-platform programming language.

The development of FORTRAN paralleled the early evolution of compiler technology, and many advances in the theory and design of compilers were specifically motivated by the need to generate efficient code for FORTRAN programs.

Basic Structure, Commands and Syntaxes of FORTRAN

A FORTRAN program generally consists of a main program and possibly several subprograms (i.e., functions or subroutines). The structure of a main program is:

- Program name
- Declarations
- Statements
- End

FORTRAN is not case-sensitive, so "X" and "x" are the same variable. Blank spaces are ignored in Fortran 77. If you remove all blanks in a Fortran 77 program, the program is still acceptable to a compiler but almost unreadable to humans.

Fortran 77 is not a free-format language, but has a very strict set of rules for how the source code should be formatted. The most important rules are the column position rules:

- Column 1: Blank, or a "c" or "*" for comments
- Column 1-5: Blank or statement label
- Column 6: Blank or a "+" for continuation of previous line
- Column 7-72: Statements

The lines that begin with a "c" or "*" are comments and have no purpose other than to make the program more readable for humans.

Sometimes, a statement does not fit into the 66 available columns of a single line. One can then break the statement into two or more lines, and use the continuation mark in position 6. Example:

```
c The next statement goes over two physical lines
      area = 3.14159265358979
     +       *r*r
```

Any character can be used instead of the plus sign as a continuation character. It is considered good programming style to use either the plus sign or digits (using 2 for the second line, 3 for the third, and so on).

Every variable should be defined in a declaration. This establishes the type of the variable. The most common declarations are:

```
integer list of variables
real list of variables
logical list of variables
character list of variables
```

The list of variables should consist of variable names separated by commas. Each variable should be declared exactly once.

Some constants appear many times in a program. It is then often desirable to define them only once, in the beginning of the program. This is what the parameter statement is for. It also makes programs more readable. For example, the circle area program should rather have been written like this:

```
      program circle
      real r, area, pi
      parameter (pi = 3.14159)
c This program reads a real number r and prints
c the area of a circle with radius r.
      write (*,*) 'Give radius r:'
      read (*,*) r
      area = pi*r*r
      write (*,*) 'Area = ', area
      end
```

The syntax of the parameter statement is

```
      parameter (name = constant, ... , name = constant)
```

A variable assignment has the form:

```
variable_name = expression
```

The interpretation is as follows: Evaluate the right hand side and assign the resulting value to the variable on the left. The expression on the right may contain other variables, but the variable assignment does not change their value. The following example does not change the value of pi or r, only area:

```
area = pi*r*r
```

Logical expressions can only have the value .TRUE. or .FALSE. A logical expression can be formed by comparing arithmetic expressions using the following relational operators:

```
.LT. meaning <
.LE. meaning <=
.GT. meaning >
.GE. meaning >=
.EQ. meaning =
.NE. meaning /=
```

Date: ……

Some Basic Rules of Fortran

Fortran 77 is not a case-sensitive language. For example, 'A' and 'a' signify the same variable.

Column Position Rules

1. Columns 1 through 5 are reserved for statement labels. A statement label may be located anywhere within columns 1 through 5. A letter C or an * placed in column 1 indicates that the statement is a comment.
2. Column 6 is used to indicate that the statements is a continuation of the previous statement/line. A FORTRAN 77 statement may be up to 40 lines long!
3. Columns 7-72 contain the FORTRAN instructions. Instructions may be placed freely anywhere within this area. Indentation was a good idea in FORTRAN 77 just as it is now in FORTRAN 90.
4. Columns 73-80 are ignored by the compiler and may be used by the programming for any desired purpose. In the days when programs were saved on decks (yes, I said decks) of punched cards, this field was used to number the cards to ensure they were fed in the correct order.

Character Set

The character set consists of the following:

- Uppercase and lowercase letters: A - Z and a – z
- Numerals/digits: 0 – 9
- Special characters:

The FORTRAN 77 special characters (<SPC>, `=', `+', `-', `*', `/', `(', `)', `,', `.', `$', `'', and `:')

Fortran Constants

A literal constant is a piece of information whose value cannot change throughout the program unit. In other words, a number or a string of Fortran characters is called a constant. Numbers are called **numeric constants** and a string of characters is called a **character constant**. The form of the string representing a constant determines the value and data type of the constant. (For a named constant, defined by a PARAMETER statement, the name defines the data type.) There are three general kinds of constants:

- Arithmetic
- Logical

- Character

Blank characters within an arithmetic or logical constant do not affect the value of the constant. Within character constants, they do affect the value. A **signed constant** is an arithmetic constant with a leading plus or minus sign. An unsigned constant is an arithmetic constant without a leading sign. For integer, real, and double-precision data, zero is neither positive nor negative. The value of a signed zero is the same as that of an unsigned zero.

Numeric constants may be integer constants, real constants, logical constants, complex constants, and so on. Integers written without the decimal point are called fixed point constants or integer constants, for example, 125, -362, etc. It must contain at least one digit. It may have a $+$ or $-$ sign with it. If there is no explicit sign preceding the constant, the constant is assumed to be positive.

Any number written with one decimal point is called a **floating-point constant**, or a **real constant**, for example, -326.74, 23.0, etc. Real constants may be written in the fractional form (say, 0.00063), or in the exponential form (6.3×10^{-4}). In the exponential form, 6.3 is the mantissa and -4 is the exponent. To express a number in the exponential form in a Fortran program, an alphabet E is written in between the mantissa and the exponent. Thus, 6.3×10^{-4} is $6.3\mathrm{E}-4$.

We will discuss the character constants afterwards.

List of Common Library Functions (in-built) in Fortran:

Function	What it does	Argument	Value
SQRT(x)	$\sqrt{x}$	Real (≥ 0)	Real
EXP(x)	e^x	Real	Real
LOG(x) or ALOG(x)	$\log_e x$	Real (> 0)	Real
LOG10(x) or ALOG10(x)	$\log_{10} x$	Real (> 0)	Real
INT(x)	Integer part of x	Real	Integer
NINT(x)	Nearest integer part of x	Real	Integer
FLOOR(x)	Greatest integer less	Real	Integer
ABS(x)	$\lvert x \rvert$	Real	Real
IABS(x)	Integer part of $\lvert x \rvert$	Real	Integer
FLOAT(n) or REAL(n)	Integer to real	Integer	Real
SIN(x)	$\sin x$	Real (x in radian)	Real
COS(x)	$\cos x$	Real (x in radian)	Real
TAN(x)	$\tan x$	Real (x in radian)	Real
ASIN(x)	$\sin^{-1} x$	Real ($-1 \leq x \leq 1$)	Real (in radian)
ACOS(x)	$\cos^{-1} x$	Real ($-1 \leq x \leq 1$)	Real (in radian)
ATAN(x)	$\tan^{-1} x$	Real ($-1 \leq x \leq 1$)	Real (in radian)
SINH(x)	$\sinh x$	Real	Real
COSH(x)	$\cosh x$	Real	Real
TANH(x)	$\tanh x$	Real	Real
ATAN2(x, y)	$\tan^{-1}(x/y)$	Real	Real (in radian)
DFLOAT(n)	Integer into double precision	Integer	Double precision
DBLE(x)	Real into double precision	Real	Double precision
MOD(m, n)	Remainder when M÷N	Integer	Integer
AINT(x)	Real with truncation	Real	Real
ANINT(x)	Nearest real with rounding off	Real	Real
DIM(x, y)	$y - \min(x, y)$	Real	Real
IDIM(i, j)	$j - \min(i, j)$	Integer	Integer
SIGN(x, y)	$\lvert x \rvert \times$ the sign of y	Real	Real
ISIGN(i, j)	$\lvert i \rvert \times$ the sign of j	Integer	Integer

List of Library Functions (in-built) in Fortran for the processing of Complex Numbers:

Function	Meaning of Function
REAL(x)	Real part of the complex number x
AIMAG(x)	Imaginary part of the complex number x
CABS(x)	Absolute value of the complex number x
CONJ(x)	Complex conjugate of x
CLOG(x)	Logarithm of the complex number x
CSQRT(x)	Square root of the complex number x
CEXP(x)	Exponential of the complex number $x = e^x$
CSIN(x)	$\sin x$ where x is a complex number
CCOS(x)	$\cos x$ where x is a complex number
CMPLX(a, b)	Refers to the complex number $a + ib$

Date: ……

The Use of Conditions in FORTRAN

An important part of any programming language is the conditional statements. The most common such statement in FORTRAN is the `if` statement. The following is a simple example of the logical if statement that finds the absolute value of `x`:

```
if (x .LT. 0) x = -x
```

The most general form of the if statement has the following form:

```
if (logical expression) then
    statements
elseif (logical expression) then
    statements
    :
    :
else
    statements
endif
```

The execution flow is from top to bottom. The conditional expressions are evaluated in sequence until one is found to be true. Then the associated statements are executed and the control resumes after the `endif`.

For repeated execution of similar things, loops are used. The do-loop is used for simple counting. Here is a simple example that prints the cumulative sums of the integers 1 through 10:

```
integer i, n, sum
  sum = 0
  n = 10
do i = 1, n
   sum = sum + i
   write(*,*) 'i =', i
   write(*,*) 'sum =', sum
enddo
```

The number 10 is a statement label. Typically, there will be many loops and other statements in a single program that require a statement label. The programmer is responsible for assigning a unique number to each label in each program (or subprogram). Recall that column positions 1-5 are reserved for statement labels. The numerical value of statement labels has no significance, so any integers can be used, in any order. Typically, most programmers use consecutive multiples of 10.

PRACTICE PROGRAMS

```
program test_2
implicit real*8 (a-h, o-z)
write(*,*)"Input the two numbers"
read (*,*) a,b
suma=a+b
diff=a-b
amag=abs(a-b)
apdt=a*b
div=a/b
write(*,*) "The sum of ", a, " and ", b, " is =", suma
write(*,*) "The difference of ", a, " and ", b, " is =", diff
write(*,*) "The magnitude of the difference of a, b is ", amag
write(*,*) "The product of ", a, " and ", b, " is =", apdt
write(*,*) "The divisor of ", a, " and ", b, " is =", div
stop
end
```

```
program increasing
implicit real*8 (a-h,o-z)
write (*,*) " insert the numbers "
read (*,*) a,b,c
if((a-b).gt.0.0) write(*,*) "a>b"
if((c-a).lt.0.0) write(*,*) "a>c"
if((b-c).gt.0.0) write(*,*) "b>c"
stop
end
```

```
      program comparison
      implicit real*8 (a-h, o-z)
      write(*,*) "Insert the two numbers"
      read(*,*)a, b
      if((a-b).eq.0.0) then
      go to 5
      else
      if((a-b).gt.0.0) then
      go to 6
      else
      if((a-b).lt.0.0) then
      go to 7
      end if
      end if
      end if
 5    write(*,*)"a = b"
 6    write(*,*)"a > b"
 7    write(*,*)"a < b"
        stop
        end
```

Date: ……

PROGRAMMING PRACTICE

```
 program sorting_of_numbers
implicit none
integer n, i, j, t
real*4 a, b
dimension a(100), b(100)

write(*,*) "How many numbers are given to sort?"
read(*,*) n

write(*,*) "Enter the numbers"
read(*,*) (b(i), i=1,n)

do i=1,n
   a(i)=b(i)
enddo
do i=1,n
   do j=1,n
      if(a(i).lt.a(j))then
        t=a(j)
        a(j)=a(i)
        a(i)=t
      endif
   enddo
enddo
write(*,*) ""
write(*,*) "In increasing order, the numbers are"
write(*,*) ""
write(*,*) (a(i),i=1,n)
write(*,*) ""
do i=1,n
   do j=1,n
      if(b(i).gt.b(j))then
        t=b(j)
        b(j)=b(i)
        b(i)=t
      endif
   enddo
enddo
write(*,*) ""
write(*,*) "In decreasing order, the numbers are"
write(*,*) ""
write(*,*) (b(i),i=1,n)
write(*,*) ""

stop
end
```

For repeated execution of similar things, loops are used. The do-loop is used for simple counting. Here is a simple example that prints the cumulative sums of the integers 1 through 10:

```
integer i, n, sum
sum = 0
n = 10
do i = 1, n
```

```
sum = sum + i
write(*,*) 'i =', i
write(*,*) 'sum =', sum
enddo
```

The number 10 is a statement label. Typically, there will be many loops and other statements in a single program that require a statement label. The programmer is responsible for assigning a unique number to each label in each program (or subprogram). Recall that column positions 1-5 are reserved for statement labels. The numerical value of statement labels has no significance, so any integers can be used, in any order. Typically, most programmers use consecutive multiples of 10.

Many scientific computations use vectors and matrices. The data type FORTRAN uses for representing such objects is the array. A one-dimensional array corresponds to a vector, while a two-dimensional array corresponds to a matrix. The simplest array is the one-dimensional array, which is just a sequence of elements stored consecutively in memory. For example, the declaration

```
real vect1(20)
```

declares vect1 as a real array of length 20. By convention, FORTRAN arrays are indexed from 1 and up. Thus, the first number in the array is denoted by `vect1(1)` and the last by `vect1(20)`. However, you may define an arbitrary index range for your arrays using the following syntax:

```
real b(0:19), weird(-162:237)
```

Here, `b` is similar to `vect1` from the previous example, except the index runs from 0 through 19, while weird is an array of length 237-(-162)+1 = 400. Each element of an array can be thought of as a separate variable. You reference the i'th element of array a by `a(i)`. Here is a code segment that stores the squares of the numbers 1 through 10 in the array `sq`:

```
integer i, sq(10)
do i = 1, 10
sq(i) = i**2
enddo
```

A common bug in FORTRAN is that the program tries to access array elements that are out of bounds or undefined. This is the responsibility of the programmer, and the FORTRAN compiler will not detect any such bugs!
Matrices are very important in linear algebra. Matrices are usually represented by two-dimensional arrays. For example, the declaration

```
real A(3,5)
```

defines a two-dimensional array of 3*5=15 real numbers. It is useful to think of the first index as the row index, and the second as the column index. Hence we get the graphical picture:

```
(1,1) (1,2) (1,3) (1,4) (1,5)
(2,1) (2,2) (2,3) (2,4) (2,5)
(3,1) (3,2) (3,3) (3,4) (3,5)
```

It is quite common in FORTRAN to declare arrays that are larger than the matrix we want to store. (This is because FORTRAN does not have dynamic storage allocation.) This is perfectly legal. Example:

```
real A(3,5)
integer i,j
c
c We will only use the upper 3 by 3 part of this array.
c
do j = 1, 3
do i = 1, 3
A(i,j) = real(i)/real(j)
enddo
enddo
```

The elements in the sub-matrix `A(1:3,4:5)` are undefined. It is not be assumed that these elements are initialized to zero by the compiler (some compilers will do this, but not all).

FORTRAN functions are quite similar to mathematical functions. They both take a set of input arguments (variables) and return a value of some type. Fortran 77 has some intrinsic (built-in) functions. The following example illustrates how to use a function:

```
x = cos(pi/3.0)
```

Here `cos` is the cosine function, so `x` will be assigned the value 0.5 assuming pi has been correctly defined; Fortran 77 has no built-in constants. There are many intrinsic functions in Fortran 77. Some of the most common are:

```
abs absolute value
sqrt square root
sin sine
tan tangent
atan arctangent
exp exponential (natural)
log logarithm (natural)
```

An important part of any computer program is the handling of input and output. In our examples so far, we have already used the two most common FORTRAN constructs for this: `read` and `write`. Fortran I/O can be quite complicated, so we will only describe some simpler cases in this hand-out. `Read` is used for input, while `write` is used for output. A simple form is

```
read (unit no, format no) list-of-variables
write(unit no, format no) list-of-variables
```

The unit number can refer to either standard input, standard output, or a file. The format number refers to a label for a format statement. It is possible to simplify these statements further by using asterisks (*) for some arguments, like we have done in most of our examples so far. This is sometimes called list directed read/write.

```
read (*,*) list-of-variables
write(*,*) list-of-variables
```

The first statement will read values from the standard input and assign the values to the variables in the variable list, while the second one writes to the standard output. It is also possible to read from or write to files. Before you can use a file you have to open it. The command is

```
open (list-of-specifiers)
```

The most common specifiers are:

```
unit = u
file = filename
```

where u is the unit number in the range 1-99 that denotes this file (the programmer may choose any number but he/she has to make sure it is unique) and filename is a character string denoting the file name. After a file has been opened, you can access it by read and write statements. When you are done with the file, it should be closed by the statement close (list-of-specifiers)

For example, you are given a data file with xyz coordinates for a bunch of points. The number of points is given on the first line. The file name of the data file is `points.dat`. Here is a short program that reads the data into 3 arrays `x,y,z`:

```
      program inpdat
c
c The program reads n points from a data file & stores them in
c 3 arrays x, y, z.
c
      integer nmax
      parameter (nmax=1000)
      real x(nmax), y(nmax), z(nmax)
c Open the data file
      open (unit=20, file='points.dat')
c Read the number of points
      read(20,*) n
      if (n.GT.nmax) then
      write(*,*) 'Error: n = ', n, 'is larger than nmax =', nmax
      goto 9999
      endif
c Loop over the data points
      do i= 1, n
      read(20,100) x(i), y(i), z(i)
      enddo
100   format (3(F10.4))
c Close the file
      close (20)
c Now we can process the data somehow...
9999 stop
      end
```

Date: ……

More on FORTRAN Structure

When a program is more than a few hundred lines long, it gets hard to follow. FORTRAN codes that solve real problems often have tens of thousands of lines. The only way to handle such big codes is to use a modular approach and split the program into many separate smaller units called subroutines. The syntax is very similar to the structure of the main program except that it is identified as a subroutine and there is a return statement before the end. The following is an example of a simple subroutine used to swap two integers.

```
      subroutine iswap (a,b)
c input/output variables
      integer a, b
c local variables
      integer tmp
      tmp = a
      a = b
      b = tmp
      return
      end
```

Note that there are two blocks of variable declarations here. First, we declare the input/output parameters, i.e. the variables that are common to both the caller and the callee. Then we declare the local variables, i.e. the variables that can only be used within this subprogram. We can use the same variable names in different subroutines and the compiler will know that they are different variables that just happen to have the same names. Subroutines are invoked using the word call before their names and parameters.

```
      program callex
      integer m, n
      m = 1
      n = 2
      call iswap(m,n)
      write(*,*) m, n
      end
```

When one has written a FORTRAN program, one should save it in a file that has the extension .f Before one can execute the program, one needs to translate source code into machine readable form. This is done by a special program called the compiler. The Unix command that typically runs the Fortran 77 compiler is f77. (Note: The FORTRAN compiler used on cgate, however, is invoked by the command xlf.) The compiler translates source code into object code and the linker/loader makes this into an executable. The default output from the compilation is given the somewhat cryptic name a.out, but you can choose another name if you wish using the -o option. For example,

```
f77 circle.f -o circle.out
```

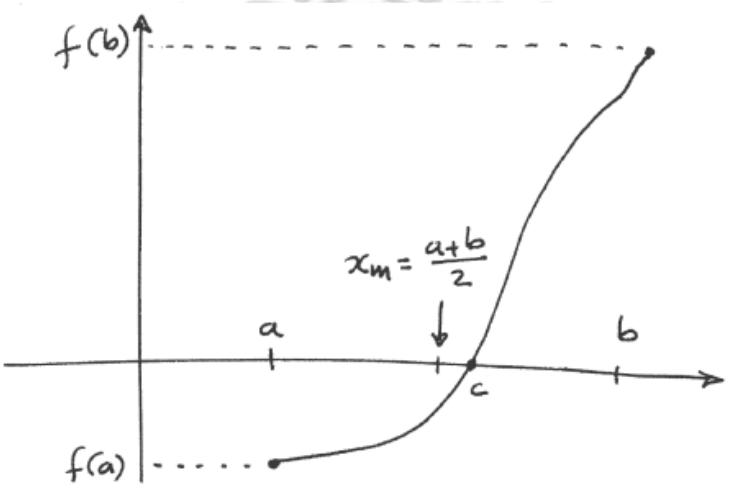
will compile the file `circle.f` and save the executable in the file `circle.out` (rather than the default `a.out`).

Date: ……

Finding the roots (or zeros) of equations (or polynomials): The Bisection Method

The *bisection method* is a technique for finding a solution to the nonlinear equation $f(x) = 0$, which can be used provided that the function f is continuous. The motivation for this technique is drawn from Bolzano's theorem for continuous functions:

- Theorem (Bolzano): If the function $f(x)$ is continuous in $[a, b]$ and $f(a)f(b) < 0$ (i.e. the function f has values with different signs at a and b), then a value $c \in (a, b)$ exists such that $f(c) = 0$.



The bisection algorithm attempts to locate the value c where the plot of f crosses over zero, by checking whether it belongs to either of the two sub-intervals $[a, x_m], [x_m, b]$, where x_m is the midpoint.

$$x_m = \frac{a+b}{2}$$

The algorithm proceeds as follows:

- If $f(x_m) = 0$, we have our solution (x_m) and the algorithm terminates.
- In the much more likely case that $f(x_m) \neq 0$ we observe that $f(x_m)$ must have the opposite sign than one of $f(a)$ or $f(b)$ (since they have opposite signs themselves). Thus, either $f(a)f(x_m) < 0$, or $f(x_m)f(b) < 0$.

We pick whichever of these 2 intervals satisfies this condition, and continue the bisection process with it.

ALGORITHM FOR THE BISECTION METHOD:

1. Define the function.
2. Define the domain (a, b) for which the root has to be found out.
3. Define the desired accuracy for the root.
4. Find out $f(a)$ and $f(b)$.
5. Define $fab = f(a) * f(b)$ and check whether fab is negative or not.
6. If fab is positive, the root does not exist in the domain (a, b).
7. If fab is negative, proceed to find the actual root.
8. Define $c = (a + b)/2$.
9. Determine $fc = f(c)$ and check which one among $f(a) * f(c)$ or $f(b) * f(c)$ is negative.
10. Choose the negative one, and repeat steps 8 and 9, till you reach the desired accuracy.

FORTRAN Program for the Bisection Method:

```
      program bisection_method
      implicit real*8 (a-h, o-z)
      write(*,*) "What is the domain for root finding?"
      read(*,*) a, b
      write(*, *) "How much accuracy do you want?"
      read(*,*) err

      fa = f(a)
      fb = f(b)
      fp = fa*fb
      if (fp.gt.0.0) go to 100
15    c = (a+b)/2
      fc = f(c)
      if (abs(fc).le.err) then
      write(*,20) c
20    format(5x, "The root is", f8.4)
      go to 200
      else
      fp = fa*fc
      if (fp.lt.0.0) then
      b = c
      fb = fc
      go to 15
      else
      a = c
      fa = fc
      go to 15
      end if
      end if
      go to 200
100   write(*,*) "Root does not exist between", a, " and", b
200   stop
      end

      function f(x)
      real*8 x
c       Choose any one of the functions
      f = 3.0*x + sin(x) - exp(x)
c     f = exp(x)*log(x) - x**2
c     f = x**3 - 6.0*x**2 + 11.0*x - 6.0
      return
      end
```

Date: ……

Numerical Differentiation: with the Richardson extrapolation

The first question that comes up to mind is: why do we need to approximate derivatives at all? After all, we do know how to analytically differentiate every function. Nevertheless, there are several reasons as of why we still need to approximate derivatives:

- Even if there exists an underlying function that we need to differentiate, we might know its values only at a sampled data set without knowing the function itself.
- There are some cases where it may not be obvious that an underlying function exists and all that we have is a discrete data set. We may still be interested in studying changes in the data, which are related, of course, to derivatives.
- There are times in which exact formulas are available but they are very complicated to the point that an exact computation of the derivative requires a lot of function evaluations. It might be significantly simpler to approximate the derivative instead of computing its exact value.
- When approximating solutions to ordinary (or partial) differential equations, we typically represent the solution as a discrete approximation that is defined on a grid. Since we then have to evaluate derivatives at the grid points, we need to be able to come up with methods for approximating the derivatives at these points, and again, this will typically be done using only values that are defined on a lattice. The underlying function itself (which in this case is the solution of the equation) is unknown.

A simple approximation of the first derivative is

$$f'(x) = \lim_{h\to 0} \frac{f(x+h) - f(x)}{h} \approx \frac{f(x+h) - f(x)}{h} \dots\dots\dots\dots (1)$$

where we assume that $h > 0$. For linear functions the above equation is actually an exact expression for the derivative. For almost all other functions, it is not the exact derivative, but only an approximation to it.

Let's compute the approximation error. We write a Taylor expansion of $f(x + h)$ about x, that is,

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2} f''(\xi), \qquad \xi \in (x, x+h) \dots\dots\dots\dots (2)$$

For such an expansion to be valid, we assume that $f(x)$ has two continuous derivatives. The above Taylor expansion means that we can now replace the approximation in the first equation with an exact formula of the form

$$f'(x) = \frac{f(x+h) - f(x)}{h} - \frac{h^2}{2} f''(\xi), \qquad \xi \in (x, x+h) \dots\dots\dots\dots (3)$$

Since this approximation of the derivative at x is based on the values of the function at x and $x + h$, the approximation in the first equation is called a **forward differencing** or one-sided differencing. The approximation of the derivative at x that is based on the values of the function at $x - h$ and x, that is,

$$f'(x) \approx \frac{f(x) - f(x-h)}{h}$$

is called a **backward differencing** (which is obviously also a one-sided differencing formula). The second term in Eq. (3) is the **error term**.

Let us illustrate this by taking an example. Say, $f(x) = \ln x$, let us compute the value of its derivative at $x_0 = 1.8$ ($f'_{\text{exact}} = 0.555$).

h	Forward difference, $f'(x) = \frac{f(x+h) - f(x)}{h}$	Backward difference, $f'(x) = \frac{f(x) - f(x-h)}{h}$	Central difference, $f'(x) = \frac{f(x+h) - f(x-h)}{2h}$
0.10	0.540	0.571	0.556

0.05	0.547	0.563	0.556
0.01	0.554	0.557	0.555

∴ The central difference has a faster rate of convergence.

```
      program derivative_richardson
      parameter (id=15)
      dimension d(id,id)
      external f
      write(*,*) "Insert the value of h"
      read(*,*) h
      write(*,*) "Insert the value of n"
      read(*,*) n
      pi3 = 4.0*atan(1.0)/3.0
      call deriv(f,pi3,n,h,d,id)
      stop
      end
      function f(x)
      f = sin(x)
      return
      end
      subroutine deriv(f,x,n,h,d,id)
      dimension d(id,n)
      do 3 i = 1, n
      d(i,1) = (f(x+h)-f(x-h))/(2.0*h)
      q = 4.0
      do 2 j = 1, i-1
      d(i,j+1) = d(i,j)+(d(i,j)-d(i-1,j))/(q-1.0)
      q = 4.0*q
2         continue
      write(*,4) (d(i,j), j=1,i)
      h = h/2.0
3     continue
4     format(5x,5f8.4)
      return
      end
```

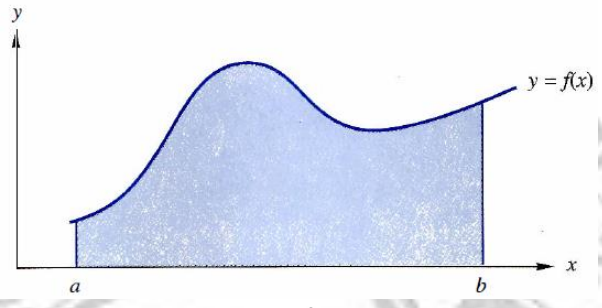
Date: ……

NUMERICAL INTEGRATION: GENERAL THEORY

One problem in which numerical methods are often used is that of approximating an integral,

$$\int_a^b f(x)dx$$

If $f(x)$ is non-negative in the interval $[a, b]$, this corresponds to finding the area of the region under the graph $y = f(x)$ from $x = a$ to $x = b$.

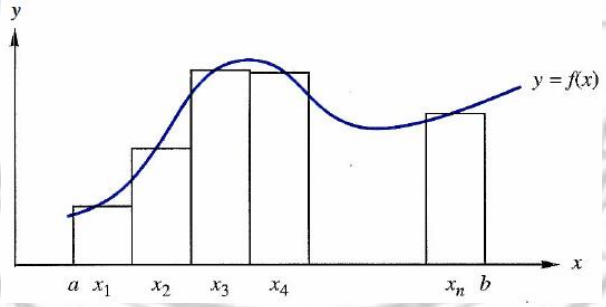


The exact value of this integral can be obtained by finding an anti-derivative F of the function f, that is, a function F, whose derivative $F' = f$, and evaluate it in between a and b:

$$\int_a^b f(x)dx = F(b) - F(a)$$

For many functions f it is difficult to find an anti-derivative, and in such cases the integral must be approximated. The common methods for approximating the area of the region under the graph of a non-negative function begin by dividing the interval $[a, b]$ into n sub-intervals. The length of each sub-interval is, $\Delta x = (b - a)/n$.

∴ We select $n - 1$ equally spaced points $x_1, x_2, \dots, x_{n-1}$ between a and b. Drawing vertical lines through these points then sub-divides the region into n strips.



The area of each of these strips is then approximated, and the sum of these approximate values provides an approximation to the total area. It may also be used to approximate the integral of a function whose graph falls below the x axis. In this case, the integral does not give the total area between the curve and the axis, rather, it gives the area of the region(s) above the axis minus the area of the region(s) below the axis.

The Rectangle Method

In this method, the area of each strip is approximated by a rectangle having one of the sub-intervals as a base and whose height is given by the value of the function at some selected point (here the mid-points, $m_1, m_2, \dots, m_n$) of the sub-interval. The sum of the areas of these rectangles are,

$$f(\mathrm{m}_1)\Delta x + f(m_2)\Delta x + \cdots + f(m_n)\Delta x = [f(\mathrm{m}_1) + f(m_2) + \cdots + f(m_n)]\Delta x$$

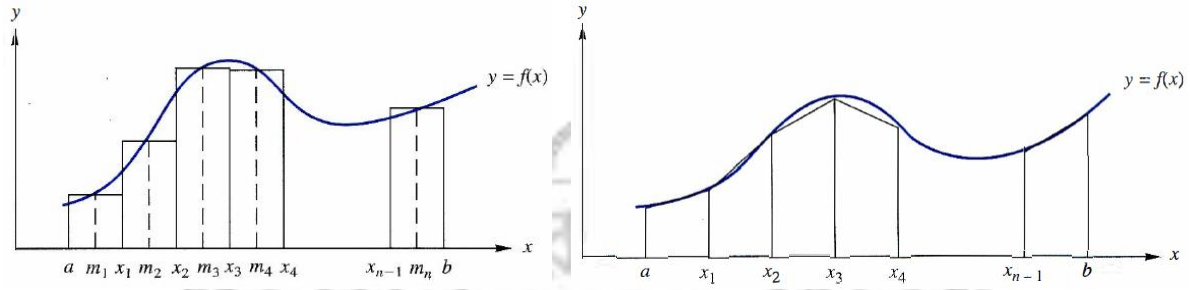
That is,

$$\left[\sum_{i=1}^{n} f(m_i)\right]\Delta x$$

is an approximation to the area under the curve. Another method of numerical integration is the Trapezoidal Rule.

The Trapezoidal Rule

An alternative to the rectangle method for approximating an integral is to replace the top boundary of each rectangle with a line joining the two points on the graph of $y = f(x)$, determined by the points of subdivision, thus forming trapezoids.



Trapezoids usually yield a better approximation than do rectangles, because their boundaries fit the graph paper better than do the horizontal segments of rectangles. Area of a trapezoid with parallel bases of lengths b_1 and b_2 and height h is

$$\frac{h}{2}(b_1 + b_2)$$

Bases of the trapezoids are the vertical segments from the x axis to points on the graph. The height of each trapezoid is $\Delta x = x_i - x_{i-1}$.

∴ The sum of the areas of the trapezoids is

$$\frac{\Delta x}{2}[f(a) + f(x_1)] + \frac{\Delta x}{2}[f(x_1) + f(x_2)] + \frac{\Delta x}{2}[f(x_2) + f(x_3)] + \cdots + \frac{\Delta x}{2}[f(x_{n-1}) + f(b)]$$

which simplifies to,

$$\frac{\Delta x}{2}[f(a) + 2f(x_1) + 2f(x_2) + \cdots + 2f(x_{n-1}) + f(b)] = \Delta x\left[\frac{f(a) + f(b)}{2} + \sum_{i=1}^{n-1} f(x_i)\right]$$

We will implement this to programming.

Simpson's $\left(\frac{1}{3}\right)$ Rule

Simpson's Rule, named after Thomas Simpson though also used by Kepler (Kepler's barrel rule), a century before, was a way to approximate integrals without having to deal with lots of narrow rectangles (which also implies lots of decimal calculations). Its strength is that, although rectangles and trapezoids work better for linear functions, Simpson's rule works quite well on curves. Simpson's rule is based on the fact that given any three points; one can find the equation of a quadratic through those points. Say, we have three points: $(3,\ 12)$, $(1,\ 5)$, and $(5,\ 9)$. Starting with

$$(3,\ 12)$$
$$x\ \ y$$

and using $y = ax^2 + bx + c$, we can write: $12 = a(3)^2 + b(3) + c$, that is $12 = 9a + 3b + c$. Similarly, with the other two points, $(1,\ 5)$, and $(5,\ 9)$, we can write,

$$5 = a + b + c$$

and

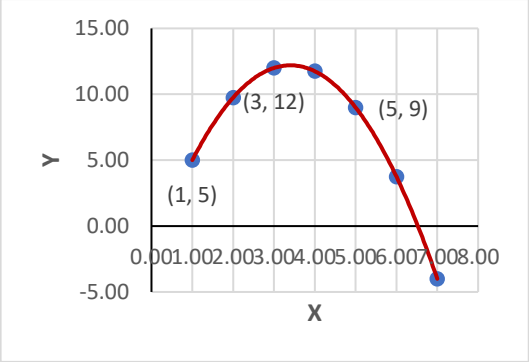
$$9 = 25a + 5b + c,$$

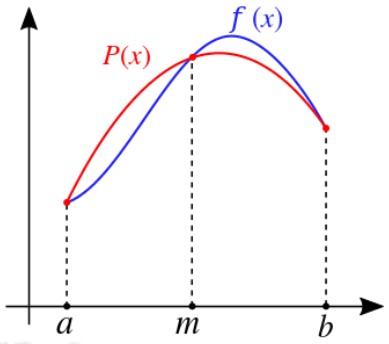
respectively. Then we can solve this system of equations for a, b, and c, and get the equation of the quadratic. This gives,

$$a = -1.25$$
$$b = 8.5$$
$$c = -2.25$$

Then with these values of a, b, and c, we write the equation for the quadratic as,

$$y = -1.25x^2 + 8.5x - 2.25$$





This fact inspired Simpson to approximate integrals using quadratics, as follows. If you want to integrate $f(x)$ over the interval from a to b,

- Find $f(a)$, $f(b)$, and $f(m)$ where m is the midpoint of the interval.
- Find a quadratic $P(x)$ that goes through the same three points.

Since quadratics are easy to integrate, we can just integrate the quadratic over the interval. It ends up being a very good approximation, but it is also a lot of math! Fortunately, there's a nice shortcut. It turns out that the integral of the quadratic over the interval $[a,\ b]$ always comes out to

$$\frac{(b-a)}{6}[f(a)+4f(m)+f(b)]$$

where $f(a)$, $f(m)$ and $f(b)$ were the values of the original function at a, m, and b. We do not need the quadratic at all.

∴ Simpson's rule uses a second order polynomial for the integrand. Say,

$$I=\int_a^b f(x)dx$$

The integrand $f(x)$ is approximated by a second order polynomial, $f_2(x)$, say. That is,

$$I=\int_a^b f(x)dx \approx \int_a^b f_2(x)dx$$

Thus, $f_2(x)=a_0+a_1x+a_2x^2$ is a second order polynomial. We choose three points:

$$(a,f(a)),\left(\frac{a+b}{2},f\left(\frac{a+b}{2}\right)\right),(b,f(b))$$

as the points of the function to evaluate a_0, a_1 and a_2. Note that, $(a+b)/2 \equiv m$. Therefore,

$$f(a)=f_2(a)=a_0+a_1a+a_2a^2$$

$$f\left(\frac{a+b}{2}\right)=f_2\left(\frac{a+b}{2}\right)=a_0+a_1\left(\frac{a+b}{2}\right)+a_2\left(\frac{a+b}{2}\right)^2$$

$$f(b)=f_2(b)=a_0+a_1b+a_2b^2$$

Solving the above three equations for the unknowns a_0, a_1 and a_2, we get,

$$a_0=\frac{a^2f(b)+abf(b)-4abf\left(\frac{a+b}{2}\right)+abf(a)+b^2f(a)}{a^2-2ab+b^2}$$

$$a_1=\frac{af(a)-4af\left(\frac{a+b}{2}\right)+3af(b)+3bf(a)-4bf\left(\frac{a+b}{2}\right)+bf(b)}{a^2-2ab+b^2}$$

$$a_2=\frac{2\left(f(a)-2f\left(\frac{a+b}{2}\right)+f(b)\right)}{a^2-2ab+b^2}$$

Then,

$$I \approx \int_a^b f_2(x)dx=\int_a^b (a_0+a_1x+a_2x^2)\,dx=\left[a_0x+a_1\frac{x^2}{2}+a_2\frac{x^3}{3}\right]_a^b$$

$$\therefore I = a_0(b-a) + a_1\frac{b^2-a^2}{2} + a_2\frac{b^3-a^3}{3}$$

Now, substituting the values of a_0, a_1 and a_2 give,

$$I \approx \int_a^b f_2(x)dx = \frac{b-a}{6}\left[f(a) + 4f\left(\frac{a+b}{2}\right) + f(b)\right]$$

In the above treatment, the interval $[a, b]$ is broken into two segments (a to m, and m to b), the width of the segment is,

$$h = \frac{b-a}{2} \Rightarrow \frac{b-a}{6} = \frac{h}{3}$$

Hence,

$$I \approx \int_a^b f_2(x)dx = \frac{b-a}{6}\left[f(a) + 4f\left(\frac{a+b}{2}\right) + f(b)\right] = \frac{h}{3}\left[f(a) + 4f\left(\frac{a+b}{2}\right) + f(b)\right]$$

This is Simpson's $1/3$ rule.

```
      program rectangle_1
      implicit real*8 (a-h, o-z)
      integer n, i
      write(*,*)'Enter the limits of integration'
      read(*,*) a, b
      write(*,*)'Enter the no. of sub-divisions'
      read(*,*) n
      delx = (b-a)/real(n)

      sum=0.0
      amid=a+delx/2.0

      do 20 i=1,n
         y=f(amid)
         sum=sum+y
         amid=amid+delx
20    continue
      sum=delx*sum
      write(*,10)'Approx. value using ', n,' sub-intervals is ',sum
10    format(a,i5,a,f12.3)
      stop
      end

      real*8 function f(x)
      real*8 x
      f=exp(x)
      return
      end
```

Date: ……

Numerical Integration: with the Trapezoidal rule

We want to construct numerical algorithms that can perform definite integrals of the form

$$I = \int_a^b f(x)dx$$

Calculating these definite integrals numerically is called numerical integration, numerical quadrature, or more simply quadrature.

We first consider the integration from 0 to h, with h small, to serve as the building blocks for integration over larger domains. We here define I_h as the following integral:

$$I_h = \int_0^h f(x)dx.$$

To perform this integral, we consider a Taylor series expansion of $f(x)$ about the value $x = h/2$:

$$f(x) = f(h/2) + (x - h/2)f'(h/2) + \frac{(x-h/2)^2}{2!}f''(h/2) + \frac{(x-h/2)^3}{3!}f'''(h/2) + \cdots$$

The **midpoint rule** makes use of only the first term in the Taylor series expansion. Here, we will determine the error in this approximation. Integrating,

$$I_h = hf(h/2) + \int_0^h \left[(x - h/2)f'(h/2) + \frac{(x-h/2)^2}{2!}f''(h/2) + \frac{(x-h/2)^3}{3!}f'''(h/2) + \frac{(x-h/2)^4}{4!}f''''(h/2) + \cdots\right]dx.$$

Changing the variables by letting $y = x - h/2$, and $dy = dx$, and simplifying the integral depending on whether the integrand is even or odd, we have

$$I_h = hf(h/2) + \int_{-h/2}^{h/2}\left[yf'(h/2) + \frac{y^2}{2!}f''(h/2) + \frac{y^3}{3!}f'''(h/2) + \frac{y^4}{4!}f''''(h/2) + \cdots\right]dy$$

$$= hf(h/2) + \int_0^{h/2}\left[y^2f''(h/2) + \frac{y^4}{12}f''''(h/2) + \cdots\right]dy.$$

The integrals that we need here are

$$\int_0^{h/2} y^2dy = \frac{h^3}{24},\ \int_0^{h/2} y^4dy = \frac{h^5}{160}$$

Therefore,

$$I_h = hf(h/2) + \frac{h^3}{24}f''(h/2) + \frac{h^5}{1920}f''''(h/2) + \cdots$$

From the Taylor series expansion of $f(x)$ about $x = h/2$, we have

$$f(0) = f(h/2) - \frac{h}{2}f'(h/2) + \frac{h^2}{8}f''(h/2) - \frac{h^3}{48}f'''(h/2) + \frac{h^4}{384}f''''(h/2) - \cdots$$

and

$$f(h) = f(h/2) + \frac{h}{2}f'(h/2) + \frac{h^2}{8}f''(h/2) + \frac{h^3}{48}f'''(h/2) + \frac{h^4}{384}f''''(h/2) + \cdots$$

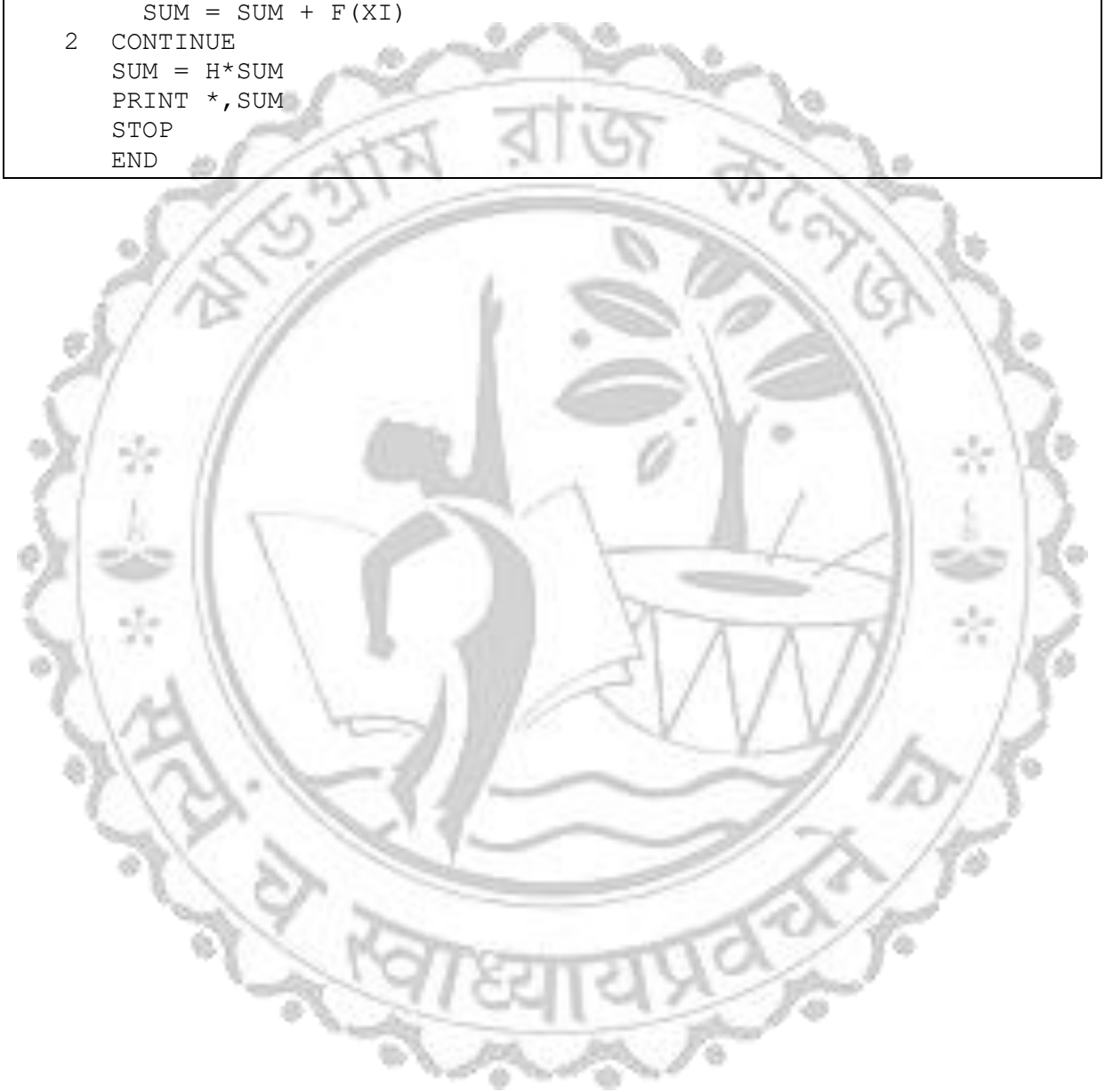
Adding and multiplying by $h/2$ we obtain

$$\frac{h}{2}[f(0) + f(h)] = \left[I_h - \frac{h^3}{24}f''(h/2) - \frac{h^5}{1920}f''''(h/2)\right] + \frac{h^3}{8}f''(h/2) + \frac{h^5}{384}f''''(h/2) + \cdots$$

and solving for I_h, we find the estimate corresponding to the **trapezoidal rule**,

$$I_h = \frac{h}{2}[f(0) + f(h)] - \frac{h^3}{12}f''(h/2) - \frac{h^5}{480}f''''(h/2) + \cdots$$

```
C
C TRAPEZOID RULE PROGRAMMING EXPERIMENT FOR AN INTEGRAL
C
      DATA  N/60/
      F(X) = 1.0/EXP(X*X)
      H = 1.0/(N-1)
      SUM = 0.5*(F(0.0) + F(1.0))
      DO 2 I=2,N-1
        XI = (I-1)*H
        SUM = SUM + F(XI)
   2  CONTINUE
      SUM = H*SUM
      PRINT *,SUM
      STOP
      END
```



Date: ……

A Fortran Program for the Solution of $ax^2 + bx + c = 0$

```
c=============================================================
c    Solution for a quadratic equation ax^2 + bx + c = 0
c    Fortran 77 demo program for students
c    method: analytic solutions
c-------------------------------------------------------------
c input: c    a, b, c - coefficients of equation
c output: c    x1, x2 - roots (can be complex)
c=============================================================
      program quad
      implicit none
      real a, b, c, x1, x2, xr, xi, D, D2
      complex x1c, x2c
      write (*,100)
       write (*,105)
      read  (*,*) a, b, c

      if(a .eq. 0.0) then
        if(b .eq. 0.0) then
c     case c = 0 (no solutions)
        write (*,101)
      else
c     case bx + c = 0
      x1 = -c/b
      write(*,102) x1
      end if

      else
c       general case ax^2 + bx + c = 0
      D2 = b*b - 4.0*a*c
      if (D2 .ge. 0.0) then
c       real roots
         D = sqrt(D2)
         x1 = ((-1.0)*b + D)/(2.0*a)
         x2 = ((-1.0)*b - D)/(2.0*a)
         write(*,103) x1, x2
      else
         D = sqrt(-1.0*D2)
         xr = b/(2.0*a)
         xi = D/(2.0*a)
          x1c = cmplx(xr, xi)
          x2c = cmplx(xr,-xi)
          write(*,*) x1c, x2c
      end if
      end if
 100  format ('solution of the quadratic equation ax^2 + bx + c = 0')
 105  format ('enter a  b  c (as floats separated by space)')
 101  format ('no solution if a = 0 and b = 0')
 102  format ('single root   x = ',f10.5)
 103  format ('real roots',' x1 = ',f10.5,' x2 = ',f10.5)
      stop
      end
```

Date: ……

A Fortran Program for the Sorting of 100 Integers

```
      program sorting_of_numbers
       implicit none
       integer n, i, j, t
       real*4 a, b
       dimension a(100), b(100)

       write(*,*) "How many numbers are given to sort?"
       read(*,*) n


       write(*,*) "Enter the numbers"
       read(*,*) (b(i), i=1,n)

       do i=1,n
          a(i)=b(i)
       enddo

       do i=1,n
          do j=1,n
             if(a(i).lt.a(j))then
               t=a(j)
               a(j)=a(i)
               a(i)=t
             endif
          enddo
       enddo

       write(*,*) ""
       write(*,*) "In increasing order, the numbers are"
       write(*,*) ""
       write(*,*) (a(i),i=1,n)
       write(*,*) ""

       do i=1,n
          do j=1,n
             if(b(i).gt.b(j))then
               t=b(j)
               b(j)=b(i)
               b(i)=t
             endif
          enddo
       enddo


       write(*,*) ""
       write(*,*) "In decreasing order, the numbers are"
       write(*,*) ""
       write(*,*) (b(i),i=1,n)
       write(*,*) ""

       stop
       end
```

Date: ……

A Fortran Program for the Multiplication of Matrices

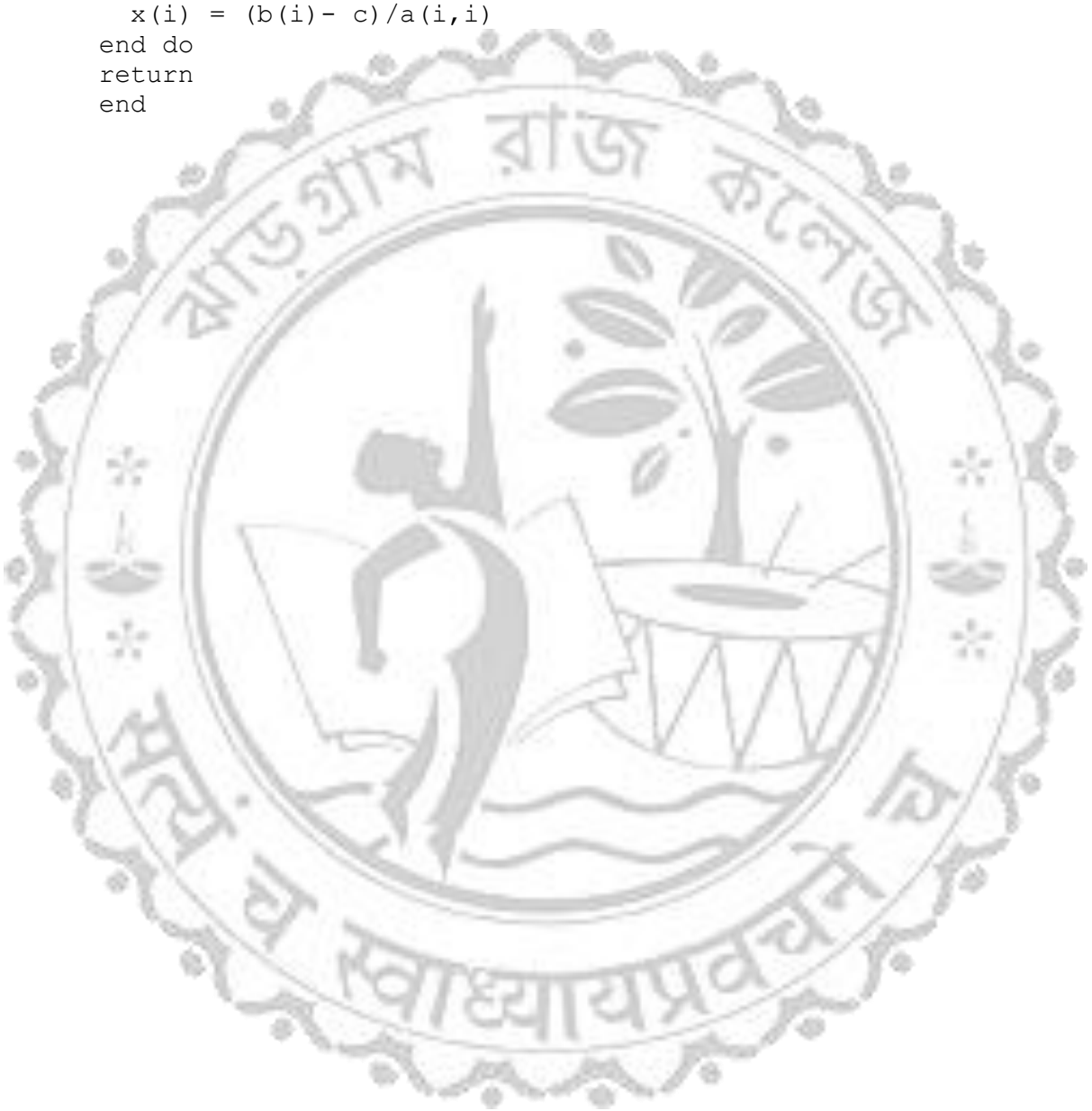
```
c      program for matrix multiplication
       program matrix_multiplication
       integer i, j, k, l, m, n1, n2
       dimension a(5,5), b(5,5), c(5,5)

       write(*,*) 'Enter the order of matrix A'
       read(*,*) m, n1
 10    write(*,*) 'Enter the order of matrix B'
       read(*,*) n2, l
       if (n1.eq.n2) go to 20
       write(*,*) 'Carefully enter the order of matrix B'
       go to 10
 20    write(*,*) 'Enter the elements of matrix A'
       do i=1,m
         read(*,*) (a(i,j),j=1,n1)
       end do
       write(*,*) 'Enter the elements of matrix B'
       do i=1,n2
         read(*,*) (b(i,j),j=1,l)
       end do

       call matmul(a,b,c,m,n1,l)

       write(*,*) 'The product of matrices A and B is:'
       do i=1,m
         write(*,*) (c(i,j),j=1,l)
       end do
       stop
       end


       subroutine matmul(a,b,c,m,n1,l)
       dimension a(m,n1), b(n1,l), c(m,l)

       write(*,*) 'The matrices A and B are:'
       do i=1,m
         write(*,*) (a(i,j),j=1,nl)
       end do
       do i=1,n1
         write(*,*) (b(i,j),j=1,l)
       end do

       do i=1,m
         do j=1,l
             c(i,j)=0.0
             do k=1,n1
                 c(i,j)=c(i,j)+(a(i,k)*b(k,j))
             end do
         end do
       end do

       return
       end
```

Date: ……

A Fortran Program for the Gaussian Elimination (no pivoting)

```
      program gaussian_elimination
      implicit none
      integer i, j, n
      real*8 a(5,5), b(5), x(5)

      open(1,file='input.txt',status='unknown')

      read(1,*)
      read(1,*) n
      read(1,*)
      do i=1,n
        read(1,*) (a(i,j),j=1,n)
      end do
      read(1,*)
      read(1,*) (b(i),i=1,n)

      write (*,200)
      do i=1,n
        write (*,201) (a(i,j),j=1,n), b(i)
      end do

      call gauss_1(a,b,x,n)

      write (*,202)
      do i = 1,n
        write (*,201)  (a(i,j),j=1,n), b(i)
      end do
      write (*,203)
      write (*,201) (x(i),i=1,n)
 200  format (' Basic elimination (Simple Gauss) '
     $        '          Matrix A and vector b')
 201  format (3f12.6,7x,3f12.6)
 202  format (/,' Matrix A and vector b after elimination')
 203  format (/,' Solutions x(n)')
      stop
      end


      subroutine gauss_1(a,b,x,n)
      implicit none
      integer i, j, k, n
      real*8 a(5,5), b(5), x(5), c

c     step 1: forward elimination
      do k=1, n-1
        do i=k+1,n
          c=a(i,k)/a(k,k)
          a(i,k) = 0.0
          b(i)=b(i)- c*b(k)
          do j=k+1,n
            a(i,j) = a(i,j)-c*a(k,j)
          end do
        end do
```

```
      end do

c     step 2: back substitution
      x(n) = b(n)/a(n,n)
      do i=n-1,1,-1
        c=0.0
        do j=i+1,n
          c=c + a(i,j)*x(j)
        end do
        x(i) = (b(i)- c)/a(i,i)
      end do
      return
      end
```



Date: ……

A Fortran Program for the Gaussian Elimination (with pivoting)

```
      program gaussian_elimination
      implicit none
      integer i, j, n
      real*8 a(5,5), b(5), x(5)

      open(1,file='input.txt',status='unknown')

      read(1,*)
      read(1,*) n
      read(1,*)
      do i=1,n
        read(1,*) (a(i,j),j=1,n)
      end do
      read(1,*)
      read(1,*) (b(i),i=1,n)

      write (*,200)
      do i=1,n
        write (*,201) (a(i,j),j=1,n), b(i)
      end do

      call gauss_2(a,b,x,n)

      write (*,202)
      do i = 1,n
        write (*,201)  (a(i,j),j=1,n), b(i)
      end do
      write (*,203)
      write (*,201) (x(i),i=1,n)
 200  format (' Basic elimination (Simple Gauss) '
     $        '        Matrix A and vector b')
 201  format (3f12.6,7x,3f12.6)
 202  format (/,' Matrix A and vector b after elimination')
 203  format (/,' Solutions x(n)')
      stop
      end


      subroutine gauss_2(a,b,x,n)
      implicit none
      integer i, j, k, l, n
      real*8 a(5,5), b(5), x(5), s(5), c, pivot, store

c     step 1: forward elimination
      do k=1, n-1

c     step 2: "scaling"
c     s(i) will have the largest element from row i
c     loop over rows
        do i=k,n
          s(i) = 0.0
c     loop over elements of row i
```

```
          do j=k, n
            s(i) = max(s(i),abs(a(i,j)))
          end do
        end do

c     step 3: "pivoting 1"
c     find a row with the largest pivoting element
        pivot = abs(a(k,k)/s(k))
        l = k
        do j=k+1,n
          if(abs(a(j,k)/s(j)) .gt. pivot) then
          pivot = abs(a(j,k)/s(j))
          l = j
          end if
        end do

c     Check if the system has a sigular matrix
        if(pivot .eq. 0.0) then
        write(*,*) ' The matrix is singular '
        return
        end if

c     step 4: "pivoting 2" interchange rows k and l (if needed)
        if (l .ne. k) then
        do j=k,n
          store = a(k,j)
          a(k,j) = a(l,j)
          a(l,j) = store
        end do
        store = b(k)
        b(k) = b(l)
        b(l) = store
        end if

c     step 5: the elimination (after scaling and pivoting)
        do i=k+1,n
          c=a(i,k)/a(k,k)
          a(i,k) = 0.0
          b(i)=b(i)- c*b(k)
          do j=k+1,n
            a(i,j) = a(i,j)-c*a(k,j)
          end do
        end do
      end do

c     step 6: back substitution
      x(n) = b(n)/a(n,n)
      do i=n-1,1,-1
        c=0.0
        do j=i+1,n
          c= c + a(i,j)*x(j)
        end do
      x(i) = (b(i)- c)/a(i,i)
      end do
      return
      end
```

Date: ……

A Fortran Program for Integration by the Simpson's Rule

```
      program simpson_2
      implicit real*8 (a-h,o-z)
      integer n, i
C      write(*,*)'Enter the limits of integration'
C      read(*,*) a, b
      a = 0.0
      b = acos(-1.0)/2.0

      delx = (b-a)/2.0
      amid = (a+b)/2.0

      sum=(delx/3.0)*(f(a)+4.0*f(amid)+f(b))
      write(*,10)'The approx. value of the integral is ',sum
10    format(a,f12.3)
      stop
      end

      real*8 function f(x)
      real*8 x
      f=log(sin(x))
      end
```

Date: ……

A Fortran Program for the Linear Least Square Fitting

```
      program linear_least_square
      implicit real*8 (a-h, o-z)
      dimension x(100),y(100),xx(100),xy(100),ynew(100)
      open(1,file='input.txt',status='unknown')
      open(2,file='output.txt',status='unknown')
      write(*,*)"Enter the no. of bivariate data points"
      read(*,*)n
      write(2,10)"The bivariate data contains ",n," data points"
      sumx=0.0
      sumy=0.0
      sumxx=0.0
      sumxy=0.0
      do i=1,n
      read(1,*)x(i),y(i)
      xx(i)=x(i)*x(i)
      xy(i)=x(i)*y(i)
      sumx=sumx+x(i)
      sumy=sumy+y(i)
      sumxx=sumxx+xx(i)
      sumxy=sumxy+xy(i)
      xavg=sumx/n
      yavg=sumy/n
      beta=(n*sumxy-sumx*sumy)/(n*sumxx-sumx**2)
      alpha=yavg-beta*xavg
      end do
      write(2,20)"Slope =",beta," Intercept =",alpha
      rewind(1)
      do i=1,n
      read(1,*)x(i),y(i)
      ynew(i)=beta*x(i)+alpha
      write(2,30)x(i),y(i),ynew(i)
      end do
10    format(a,i5,a)
20    format(a,f12.6,5x,a,f12.6)
30    format(3f12.6)
      stop
      end
```

Date: ……

A Fortran Program for the Factorial of an Integer (using a do loop in a function)

```
program demofactorial
integer n
real fact
print *, "What is n?"
read *, n
print *, "The value of", n, " factorial is", fact(n)
end

function fact(n)
integer n
real fact,p
p = 1
do i = 1, n
   p = p * i
end do
fact = p
end
```

Date: ……

A Fortran Program for the Poisson probability

```
      program poisson
      real lambda,poiss,prob
      integer n
      write(*,*)'This program calculates the Poisson probability for'
      write(*,*)'lambda = average no. of occurrences per time period'
      write(*,*)'n = no. of occurrences for which prob. to be found'
      write(*,*)'Enter lambda and n (negative values to stop)'
      read(*,*)lambda,n
 10   if(lambda.ge.0)then
         prob = poiss(lambda,n)
         write(*,*)'Poisson probability =',prob
         write(*,*)
         write(*,*)'Enter lambda and n (negative values to stop)'
         read(*,*)lambda,n
      go to 10
      end if
      stop
      end

      function poiss(lambda,n)
      integer n,factor
      real poiss,lambda
      poiss = (lambda**n*exp(-lambda))/factor(n)
      end

      function factor(n)
      integer factor,n,i
      factor = 1
      do i = 2,n
         factor = factor*i
      end do
      end
```

Date: ……

A Fortran Program to calculate the $(\partial P/\partial V)_T$ for a van der Waals gas

```
      program vdwderiv
      implicit none
      double precision h, x, xa, xb, ffor, fback, fcur, derivc,
     &                 derivf, derivb, func, step
      integer i

      write(*,*) "Give the value of H"
      read(*,*)h
      write(*,*) "Give the value of V"
      step=0.005d0
      read(*,*)x

      do i=1,50
         xa=x+h
         xb=x-h
         ffor=func(xa)
         fback=func(xb)
         fcur=func(x)
         derivf=(ffor-fcur)/h
         derivb=(fcur-fback)/h
         derivc=(ffor-fback)/(2.0d0*h)
         write(*,*)"The value of X and the derivative are"
         write(*,*)x, derivc
         x=x+step
      end do

      pause
      stop
      end

      function func(y)
      implicit none
      double precision y,func,va,vb,t,r,tc

      va=4.225d0
      vb=0.03713d0
      tc=(8.0d0*va)/(27.0d0*r*vb)
      t=300.0d0
      r=0.082d0

      func=((r*t)/(y-vb))-va/(y**2)

      return
      end
```

Date: ……

A Fortran Program to calculate the ground state energy of HeH^+ using the Hartree-Fock Theory

```
C***********************************************************************
*
C
C MINIMAL BASIS STO-3G CALCULATION ON HEH+
C
C THIS IS A LITTLE DUMMY MAIN PROGRAM WHICH CALLS HFCALC
C
C APPENDIX B: TWO-ELECTRON SELF-CONSISTENT-FIELD PROGRAM
C OF MODERN QUANTUM CHEMISTRY by
C Attila Szabo and Neil S. Ostlund
C Ed. 2nd (1989) Dover Publications INC.
C
C***********************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      IOP=2
      N=3
      R=1.4632D0
      ZETA1=2.0925D0
      ZETA2=1.24D0
      ZA=2.0D0
      ZB=1.0D0
      CALL HFCALC(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
      END

C***********************************************************************
**
      SUBROUTINE HFCALC(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
C
C DOES A HARTREE-FOCK CALCULATION FOR A TWO-ELECTRON DIATOMIC
C USING THE 1S MINIMAL STO-NG BASIS SET
C MINIMAL BASIS SET HAS BASIS FUNCTIONS 1 AND 2 ON NUCLEI A AND B
C
C IOP=0 NO PRINTING WHATSOEVER (TO OPTIMIZE EXPONENTS, SAY)
C IOP=1 PRINT ONLY CONVERGED RESULTS
C IOP=2 PRINT EVERY ITERATION
C N STO-NG CALCULATION (N=1,2 OR 3)
C R BONDLENGTH (AU)
C ZETA1 SLATER ORBITAL EXPONENT (FUNCTION 1)
C ZETA2 SLATER ORBITAL EXPONENT (FUNCTION 2)
C ZA ATOMIC NUMBER (ATOM A)
C ZB ATOMIC NUMBER (ATOM B)
C
C***********************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      IF (IOP.EQ.0) GO TO 20
      PRINT 10,N,ZA,ZB
   10 FORMAT(' ',2X,'STO-',I1,'G FOR ATOMIC NUMBERS ',F5.2,' AND ',
     $ F5.2//)
```

```
   20 CONTINUE
C CALCULATE ALL THE ONE AND TWO ELECTRON INTEGRALS
      CALL INTGRL(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
C BE INEFFICIENT AND PUT ALL INTEGRALS IN PRETTY ARRAYS
      CALL COLECT(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
C PERFORM THE SCF CALCULATION
      CALL SCF(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
      RETURN
      END

C*************************************************************************
**
      SUBROUTINE INTGRL(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
C
C CALCULATES ALL THE BASIC INTEGRALS NEEDED FOR SCF CALCULATION
C
C*************************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      COMMON/INT/S12,T11,T12,T22,V11A,V12A,V22A,V11B,V12B,V22B,
     $ V1111,V2111,V2121,V2211,V2221,V2222
      DIMENSION COEF(3,3),EXPON(3,3),D1(3),A1(3),D2(3),A2(3)
      DATA PI/3.1415926535898D0/
C THESE ARE THE CONTRACTION COEFFICIENTS AND EXPONENTS FOR
C A NORMALIZED SLATER ORBITAL WITH EXPONENT 1.0 IN TERMS OF
C NORMALIZED 1S PRIMITIVE GAUSSIANS
      DATA COEF,EXPON/1.0D0,2*0.0D0,0.678914D0,0.430129D0,0.0D0,
     $
0.444635D0,0.535328D0,0.154329D0,0.270950D0,2*0.0D0,0.151623D0,
     $ 0.851819D0,0.0D0,0.109818D0,0.405771D0,2.22766D0/
      R2=R*R
C SCALE THE EXPONENTS (A) OF PRIMITIVE GAUSSIANS
C INCLUDE NORMALIZATION IN CONTRACTION COEFFICIENTS (D)
      DO 10 I=1,N
      A1(I)=EXPON(I,N)*(ZETA1**2)
      D1(I)=COEF(I,N)*((2.0D0*A1(I)/PI)**0.75D0)
      A2(I)=EXPON(I,N)*(ZETA2**2)
      D2(I)=COEF(I,N)*((2.0D0*A2(I)/PI)**0.75D0)
   10 CONTINUE
C D AND A ARE NOW THE CONTRACTION COEFFICIENTS AND EXPONENTS
C IN TERMS OF UNNORMALIZED PRIMITIVE GAUSSIANS
      S12=0.0D0
      T11=0.0D0
      T12=0.0D0
      T22=0.0D0
      V11A=0.0D0
      V12A=0.0D0
      V22A=0.0D0
      V11B=0.0D0
      V12B=0.0D0
      V22B=0.0D0
      V1111=0.0D0
      V2111=0.0D0
      V2121=0.0D0
      V2211=0.0D0
```

```
      V2221=0.0D0
      V2222=0.0D0
C CALCULATE ONE-ELECTRON INTEGRALS
C CENTER A IS FIRST ATOM, CETER B IS SECOND ATOM
C ORIGIN IS ON CENTER A
C V12A = OFF-DIAGONAL NUCLEAR ATTRACTION TO CENTER A, ETC.
      DO 20 I=1,N
      DO 20 J=1,N
C RAP2 = SQUARED DISTANCE BETWEEN CENTER A AND CENTER P, ETC.
      RAP=A2(J)*R/(A1(I)+A2(J))
      RAP2=RAP**2
      RBP2=(R-RAP)**2
      S12=S12+S(A1(I),A2(J),R2)*D1(I)*D2(J)
      T11=T11+T(A1(I),A1(J),0.0D0)*D1(I)*D1(J)
      T12=T12+T(A1(I),A2(J),R2)*D1(I)*D2(J)
      T22=T22+T(A2(I),A2(J),0.0D0)*D2(I)*D2(J)
      V11A=V11A+V(A1(I),A1(J),0.0D0,0.0D0,ZA)*D1(I)*D1(J)
      V12A=V12A+V(A1(I),A2(J),R2,RAP2,ZA)*D1(I)*D2(J)
      V22A=V22A+V(A2(I),A2(J),0.0D0,R2,ZA)*D2(I)*D2(J)
      V11B=V11B+V(A1(I),A1(J),0.0D0,R2,ZB)*D1(I)*D1(J)
      V12B=V12B+V(A1(I),A2(J),R2,RBP2,ZB)*D1(I)*D2(J)
      V22B=V22B+V(A2(I),A2(J),0.0D0,0.0D0,ZB)*D2(I)*D2(J)
   20 CONTINUE
C CALCULATE TWO-ELECTRON INTEGRALS
      DO 30 I=1,N
      DO 30 J=1,N
      DO 30 K=1,N
      DO 30 L=1,N
      RAP=A2(I)*R/(A2(I)+A1(J))
      RBP=R-RAP
      RAQ=A2(K)*R/(A2(K)+A1(L))
      RBQ=R-RAQ
      RPQ=RAP-RAQ
      RAP2=RAP*RAP
      RBP2=RBP*RBP
      RAQ2=RAQ*RAQ
      RBQ2=RBQ*RBQ
      RPQ2=RPQ*RPQ
      V1111=V1111+TWOE(A1(I),A1(J),A1(K),A1(L),0.0D0,0.0D0,0.0D0)
     $ *D1(I)*D1(J)*D1(K)*D1(L)
      V2111=V2111+TWOE(A2(I),A1(J),A1(K),A1(L),R2,0.0D0,RAP2)
     $ *D2(I)*D1(J)*D1(K)*D1(L)
      V2121=V2121+TWOE(A2(I),A1(J),A2(K),A1(L),R2,R2,RPQ2)
     $ *D2(I)*D1(J)*D2(K)*D1(L)
      V2211=V2211+TWOE(A2(I),A2(J),A1(K),A1(L),0.0D0,0.0D0,R2)
     $ *D2(I)*D2(J)*D1(K)*D1(L)
      V2221=V2221+TWOE(A2(I),A2(J),A2(K),A1(L),0.0D0,R2,RBQ2)
     $ *D2(I)*D2(J)*D2(K)*D1(L)
      V2222=V2222+TWOE(A2(I),A2(J),A2(K),A2(L),0.0D0,0.0D0,0.0D0)
     $ *D2(I)*D2(J)*D2(K)*D2(L)
   30 CONTINUE
      IF (IOP.EQ.0) GO TO 90
      PRINT 40
   40 FORMAT(3X,'R',10X,'ZETA1',6X,'ZETA2',6X,'S12',8X,'T11'/)
      PRINT 50, R,ZETA1,ZETA2,S12,T11
   50 FORMAT(5F11.6//)
```

```
      PRINT 60
   60 FORMAT(3X,'T12',8X,'T22',8X,'V11A',7X,'V12A',7X,'V22A'/)
      PRINT 50, T12,T22,V11A,V12A,V22A
      PRINT 70
   70 FORMAT(3X,4HV11B,7X,4HV12B,7X,4HV22B,7X,'V1111',6X,'V2111'/)
      PRINT 50, V11B,V12B,V22B,V1111,V2111
      PRINT 80
   80 FORMAT(3X,5HV2121,6X,5HV2211,6X,5HV2221,6X,5HV2222/)
      PRINT 50, V2121,V2211,V2221,V2222
   90 RETURN
      END

C*************************************************************
**
      FUNCTION F0(ARG)
C
C CALCULATES THE F FUNCTION
C FO ONLY (S-TYPE ORBITALS)
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DATA PI/3.1415926535898D0/
      IF (ARG.LT.1.0D-6) GO TO 10
C F0 IN TERMS OF THE ERROR FUNCTION
      F0=DSQRT(PI/ARG)*DERFOTHER(DSQRT(ARG))/2.0D0
      GO TO 20
C ASYMPTOTIC VALUE FOR SMALL ARGUMENTS
   10 F0=1.0D0-ARG/3.0D0
   20 CONTINUE
      RETURN
      END

C*************************************************************
**
      FUNCTION DERFOTHER(ARG)
C
C CALCULATES THE ERROR FUNCTION ACCORDING TO A RATIONAL
C APPROXIMATION FROM M. ARBRAMOWITZ AND I.A. STEGUN,
C HANDBOOK OF MATHEMATICAL FUNCTIONS, DOVER.
C ABSOLUTE ERROR IS LESS THAN 1.5*10**(-7)
C CAN BE REPLACED BY A BUILT-IN FUNCTION ON SOME MACHINES
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION A(5)
      DATA P/0.3275911D0/
      DATA A/0.254829592D0,-0.284496736D0,1.421413741D0,
     $ -1.453152027D0,1.061405429D0/
      T=1.0D0/(1.0D0+P*ARG)
      TN=T
      POLY=A(1)*TN
      DO 10 I=2,5
```

```
      TN=TN*T
      POLY=POLY+A(I)*TN
   10 CONTINUE
      DERFOTHER=1.0D0-POLY*DEXP(-ARG*ARG)
      RETURN
      END

C*************************************************************
**
      FUNCTION S(A,B,RAB2)
C
C CALCULATES OVERLAPS FOR UN-NORMALIZED PRIMITIVES
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DATA PI/3.1415926535898D0/
      S=(PI/(A+B))**1.5D0*DEXP(-A*B*RAB2/(A+B))
      RETURN
      END

C*************************************************************
**
      FUNCTION T(A,B,RAB2)
C
C CALCULATES KINETIC ENERGY INTEGRALS FOR UN-NORMALIZED PRIMITIVES
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DATA PI/3.1415926535898D0/
      T=A*B/(A+B)*(3.0D0-2.0D0*A*B*RAB2/(A+B))*(PI/(A+B))**1.5D0
     $ *DEXP(-A*B*RAB2/(A+B))
      RETURN
      END

C*************************************************************
**
      FUNCTION V(A,B,RAB2,RCP2,ZC)
C
C CALCULATES UN-NORMALIZED NUCLEAR ATTRACTION INTEGRALS
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DATA PI/3.1415926535898D0/
      V=2.0D0*PI/(A+B)*F0((A+B)*RCP2)*DEXP(-A*B*RAB2/(A+B))
      V=-V*ZC
      RETURN
      END

C*************************************************************
**
```

```
      FUNCTION TWOE(A,B,C,D,RAB2,RCD2,RPQ2)
C
C CALCULATES TWO-ELECTRON INTEGRALS FOR UN-NORMALIZED PRIMITIVES
C A,B,C,D ARE THE EXPONENTS ALPHA, BETA, ETC.
C RAB2 EQUALS SQUARED DISTANCE BETWEEN CENTER A AND CENTER B, ETC.
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DATA PI/3.1415926535898D0/
      TWOE=2.0D0*(PI**2.5D0)/((A+B)*(C+D)*DSQRT(A+B+C+D))
     $ *F0((A+B)*(C+D)*RPQ2/(A+B+C+D))
     $ *DEXP(-A*B*RAB2/(A+B)-C*D*RCD2/(C+D))
      RETURN
      END

C*************************************************************
**
      SUBROUTINE COLECT(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
C
C THIS TAKES THE BASIC INTEGRALS FROM COMMON AND ASSEMBLES THE
C RELEVENT MATRICES, THAT IS S,H,X,XT, AND TWO-ELECTRON INTEGRALS
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)

COMMON/MATRIX/S(2,2),X(2,2),XT(2,2),H(2,2),F(2,2),G(2,2),C(2,2),
     $ FPRIME(2,2),CPRIME(2,2),P(2,2),OLDP(2,2),TT(2,2,2,2),E(2,2)
      COMMON/INT/S12,T11,T12,T22,V11A,V12A,V22A,V11B,V12B,V22B,
     $ V1111,V2111,V2121,V2211,V2221,V2222
C FORM CORE HAMILTONIAN
      H(1,1)=T11+V11A+V11B
      H(1,2)=T12+V12A+V12B
      H(2,1)=H(1,2)
      H(2,2)=T22+V22A+V22B
C FORM OVERLAP MATRIX
      S(1,1)=1.0D0
      S(1,2)=S12
      S(2,1)=S(1,2)
      S(2,2)=1.0D0
C USE CANONICAL ORTHOGONALIZATION
      X(1,1)=1.0D0/DSQRT(2.0D0*(1.0D0+S12))
      X(2,1)=X(1,1)
      X(1,2)=1.0D0/DSQRT(2.0D0*(1.0D0-S12))
      X(2,2)=-X(1,2)
C TRANSPOSE OF TRANSFORMATION MATRIX
      XT(1,1)=X(1,1)
      XT(1,2)=X(2,1)
      XT(2,1)=X(1,2)
      XT(2,2)=X(2,2)
C MATRIX OF TWO-ELE CTRON INTEGRALS
      TT(1,1,1,1)=V1111
      TT(2,1,1,1)=V2111
      TT(1,2,1,1)=V2111
```

```
      TT(1,1,2,1)=V2111
      TT(1,1,1,2)=V2111
      TT(2,1,2,1)=V2121
      TT(1,2,2,1)=V2121
      TT(2,1,1,2)=V2121
      TT(1,2,1,2)=V2121
      TT(2,2,1,1)=V2211
      TT(1,1,2,2)=V2211
      TT(2,2,2,1)=V2221
      TT(2,2,1,2)=V2221
      TT(2,1,2,2)=V2221
      TT(1,2,2,2)=V2221
      TT(2,2,2,2)=V2222
      IF (IOP.EQ.0) GO TO 40
      CALL MATOUT(S,2,2,2,2,4HS   )
      CALL MATOUT(X,2,2,2,2,4HX   )
      CALL MATOUT(H,2,2,2,2,4HH   )
      PRINT 10
   10 FORMAT(//)
      DO 30 I=1,2
      DO 30 J=1,2
      DO 30 K=1,2
      DO 30 L=1,2
      PRINT 20, I,J,K,L,TT(I,J,K,L)
   20 FORMAT(3X,1H(,4I2,2H ),F10.6)
   30 CONTINUE
   40 RETURN
      END
C*************************************************************************
**
      SUBROUTINE SCF(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
C
C PERFORMS THE SCF ITERATIONS
C
C*************************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)

COMMON/MATRIX/S(2,2),X(2,2),XT(2,2),H(2,2),F(2,2),G(2,2),C(2,2),
     $ FPRIME(2,2),CPRIME(2,2),P(2,2),OLDP(2,2),TT(2,2,2,2),E(2,2)
      DATA PI/3.1415926535898D0/
C CONVERGENCE CRITERION FOR DENSITY MATRIX
      DATA CRIT/1.0D-4/
C MAXIMUM NUMBER OF ITERATIONS
      DATA MAXIT/25/
C ITERATION NUMBER
      ITER=0
C USE CORE-HAMILTONIAN FOR INITIAL GUESS AT F, I.E. (P=0)
      DO 10 I=1,2
      DO 10 J=1,2
   10 P(I,J)=0.0D0
      IF (IOP.LT.2) GO TO 20
      CALL MATOUT(P,2,2,2,2,4HP   )
C START OF ITERATION LOOP
```

```
   20 ITER=ITER+1
      IF (IOP.LT.2) GO TO 40
      PRINT 30, ITER
   30 FORMAT(/,4X,28HSTART OF ITERATION NUMBER = ,I2)
   40 CONTINUE
C FORM TWO-ELECTRON PART OF FOCK MATRIX FROM P
      CALL FORMG
      IF (IOP.LT.2) GO TO 50
      CALL MATOUT(G,2,2,2,2,4HG   )
   50 CONTINUE
C ADD CORE HAMILTONIAN TO GET FOCK MATRIX
      DO 60 I=1,2
      DO 60 J=1,2
      F(I,J) = H(I,J)+G(I,J)
   60 CONTINUE
C CALCULATE ELECTRONIC ENERGY
      EN=0.0D0
      DO 70 I=1,2
      DO 70 J=1,2
      EN=EN+0.5D0*P(I,J)*(H(I,J)+F(I,J))
   70 CONTINUE
      IF (IOP.LT.2) GO TO 90
      CALL MATOUT(F,2,2,2,2,4HF   )
      PRINT 80, EN
   80 FORMAT(///,4X,20HELECTRONIC ENERGY = ,D20.12)
   90 CONTINUE
C TRANSFORM FOCK MATRIX USING G FOR TEMPORARY STORAGE
      CALL MULT(F,X,G,2,2)
      CALL MULT(XT,G,FPRIME,2,2)
C DIAGONALIZE TRANSFORMED FOCK MATRIX
      CALL DIAG(FPRIME,CPRIME,E)
C TRANSFORM EIGENVECTORS TO GET MATRIX C
      CALL MULT(X,CPRIME,C,2,2)
C FORM NEW DENSITY MATRIX
      DO 100 I=1,2
      DO 100 J=1,2
C SAVE PRESENT DENSITY MATRIX
C BEFORE CREATING NEW ONE
      OLDP(I,J)=P(I,J)
      P(I,J)=0.0D0
      DO 100 K=1,1
      P(I,J)=P(I,J)+2.0D0*C(I,K)*C(J,K)
  100 CONTINUE
      IF (IOP.LT.2) GO TO 110
      CALL MATOUT(FPRIME,2,2,2,2,"F'  ")
      CALL MATOUT(CPRIME,2,2,2,2,"C'  ")
      CALL MATOUT(E,2,2,2,2,'E   ')
      CALL MATOUT(C,2,2,2,2,'C   ')
      CALL MATOUT(P,2,2,2,2,'P   ')
  110 CONTINUE
C CALCULATE DELTA
      DELTA=0.0D0
      DO 120 I=1,2
      DO 120 J=1,2
      DELTA=DELTA+(P(I,J)-OLDP(I,J))**2
  120 CONTINUE
```

```
      DELTA=DSQRT(DELTA/4.0D0)
      IF (IOP.EQ.0) GO TO 140
      PRINT 130, DELTA
  130 FORMAT(/,4X,39HDELTA(CONVERGENCE OF DENSITY MATRIX) =
     $F10.6,/)
  140 CONTINUE
C CHECK FOR CONVERGENCE
      IF (DELTA.LT.CRIT) GO TO 160
C NOT YET CONVERGED
C TEST FOR MAXIMUM NUMBER OF ITERATIONS
C IF MAXIMUM NUMBER NOT YET REACHED
C GO BACK FOR ANOTHER ITERATION
      IF(ITER.LT.MAXIT) GO TO 20
C SOMETHING WRONG HERE
      PRINT 150
  150 FORMAT(4X,21HNO CONVERGENCE IN SCF)
      STOP
  160 CONTINUE
C CALCULATION CONVERGED IF IT GOT HERE
C ADD NUCLEAR REPULSION TO GET TOTAL ENERGY
      ENT=EN+ZA*ZB/R
      IF (IOP.EQ.0) GO TO 180
      PRINT 170, EN, ENT
  170 FORMAT(//,4X,21HCALCULATION CONVERGED,//,
     $4X,20HELECTRONIC ENERGY = ,D20.12,//,
     $4X,20HTOTAL ENERGY =      ,D20.12   )
  180 CONTINUE
      IF (IOP.NE.1) GO TO 190
C PRINT OUT THE FINAL RESULTS IF
C HAVE NOT DONE SO ALREADY
      CALL MATOUT(G,2,2,2,2,4HG   )
      CALL MATOUT(F,2,2,2,2,4HF   )
      CALL MATOUT(E,2,2,2,2,4HE   )
      CALL MATOUT(C,2,2,2,2,4HC   )
      CALL MATOUT(P,2,2,2,2,4HP   )
  190 CONTINUE
C PS MATRIX HAS MULLIKEN POPULATIONS
      CALL MULT(P,S,OLDP,2,2)
      IF(IOP.EQ.0) GO TO 200
      CALL MATOUT(OLDP,2,2,2,2,4HPS   )
  200 CONTINUE
      RETURN
      END

C*************************************************************
**
      SUBROUTINE FORMG
C
C CALCULATES THE G MATRIX FROM THE DENSITY MATRIX
C AND TWO-ELECTRON INTEGRALS
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
```

```
COMMON/MATRIX/S(2,2),X(2,2),XT(2,2),H(2,2),F(2,2),G(2,2),C(2,2),
     $FPRIME(2,2),CPRIME(2,2),P(2,2),OLDP(2,2),TT(2,2,2,2),E(2,2)
      DO 10 I=1,2
      DO 10 J=1,2
      G(I,J)=0.0D0
      DO 10 K=1,2
      DO 10 L=1,2
      G(I,J)=G(I,J)+P(K,L)*(TT(I,J,K,L)-0.5D0*TT(I,L,K,J))
   10 CONTINUE
      RETURN
      END

C*************************************************************
**
      SUBROUTINE DIAG(F,C,E)
C
C DIAGONALIZES F TO GIVE EIGENVECTORS IN C AND EIGENVALUES IN E
C THETA IS THE ANGLE DESCRIBING SOLUTION
C
C*************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION F(2,2),C(2,2),E(2,2)
      DATA PI/3.1415926535898D0/
      IF (DABS(F(1,1)-F(2,2)).GT.1.0D-20) GO TO 10
C HERE IS SYMMETRY DETERMINED SOLUTION (HOMONUCLEAR DIATOMIC)
      THETA=PI/4.0D0
      GO TO 20
   10 CONTINUE
C SOLUTION FOR HETERONUCLEAR DIATOMIC
      THETA=0.5D0*DATAN(2.0D0*F(1,2)/(F(1,1)-F(2,2)))
   20 CONTINUE
      C(1,1)=DCOS(THETA)
      C(2,1)=DSIN(THETA)
      C(1,2)=DSIN(THETA)
      C(2,2)=-DCOS(THETA)
      E(1,1)=F(1,1)*DCOS(THETA)**2+F(2,2)*DSIN(THETA)**2
     $ +F(1,2)*DSIN(2.0D0*THETA)
      E(2,2)=F(2,2)*DCOS(THETA)**2+F(1,1)*DSIN(THETA)**2
     $ -F(1,2)*DSIN(2.0D0*THETA)
      E(2,1)=0.0D0
      E(1,2)=0.0D0
C ORDER EIGENVALUES AND EIGENVECTORS
      IF (E(2,2).GT.E(1,1)) GO TO 30
      TEMP=E(2,2)
      E(2,2)=E(1,1)
      E(1,1)=TEMP
      TEMP=C(1,2)
      C(1,2)=C(1,1)
      C(1,1)=TEMP
      TEMP=C(2,2)
      C(2,2)=C(2,1)
      C(2,1)=TEMP
   30 RETURN
```

```
      END

C*************************************************************************
**
      SUBROUTINE MULT(A,B,C,IM,M)
C
C MULTIPLIES TWO SQUARE MATRICES A AND B TO GET C
C
C*************************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION A(IM,IM),B(IM,IM),C(IM,IM)
      DO 10 I=1,M
      DO 10 J=1,M
      C(I,J)=0.0D0
      DO 10 K=1,M
   10 C(I,J)=C(I,J)+A(I,K)*B(K,J)
      RETURN
      END

C*************************************************************************
**
      SUBROUTINE MATOUT(A,IM,IN,M,N,LABEL)
C
C PRINT MATRICES OF SIZE M BY N
C
C*************************************************************************
**

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION A(IM,IN)
      IHIGH=0
   10 LOW=IHIGH+1
      IHIGH=IHIGH+5
      IHIGH=MIN(IHIGH,N)
      PRINT 20, LABEL,(I,I=LOW,IHIGH)
   20 FORMAT(///,3X,5H THE ,A4,6H ARRAY,/,15X,5(10X,I3,6X)//)
      DO 30 I=1,M
   30 PRINT 40, I,(A(I,J),J=LOW,IHIGH)
   40 FORMAT(I10,5X,5(1X,D18.10))
      IF (N-IHIGH) 50,50,10
   50 RETURN
      END
```

SEMESTER-VI
(UNDER THE CBCS PATTERN)

Experiment 1: Determination of surface tension of a liquid using Stalagmometer.

Theory: A molecule in the interior of a liquid is completely surrounded by other molecules, and so on the average, it is attracted equally in all directions. On the contrary, a molecule residing on the surface of a liquid is only acted upon by a resultant inward force of attraction, since the number of molecules per unit volume is greater in the liquid (beneath the surface) than in the vapor (above the surface). Due to this effect the surface of a liquid always tends to contract into the smallest possible area. In order to extend the area of surface, it is necessary to do work in an attempt to bring the molecules from the bulk of the liquid into the surface, against the inward attractive force. The work required to increase the area of a surface of a liquid by 1 cm^2 is called the surface (free) energy. *The surface tension of a liquid is defined as the tangential force, in dynes, that acts along the surface of the liquid at right angles to a line of 1 cm length on the surface.*

The surface tension of a pure liquid/solution can be measured either by using the drop-weight or the capillary rise method. Here we implement the drop-weight (equivalent to the drop-counting) method to determine the surface tension of the supplied solution or liquid. The principle of the drop-weight method is based on the fact that when a liquid is allowed to flow through a capillary tube (thus ensuring almost streamline flow) and fall in drops from its end, the drop first remains sticking at the end of the capillary tube, but it falls down when its weight becomes just equal to the force of surface tension, acting on it.

The weight w of a drop of liquid of density ρ and volume v is given by

$$w = v\rho g.$$

If the radius of the drop be r, and if γ be the surface tension acting on it, then the force due to surface tension is $2\pi r\gamma$, where $2\pi r$ is the circumference of the liquid drop. If there are n drops in a finite volume V, then the volume of a single drop, $v = V/n$. Therefore, under the condition of equilibrium

$$2\pi r\gamma = \frac{V\rho g}{n}$$

If two different liquids of densities ρ_A and ρ_B and surface tensions γ_A and $\gamma_B$are allowed to flow in equal volumes V through the same stalagmometer, and if n_A and n_B be the number of drops that make up for the volume V, then we must have

$$2\pi r\gamma_A = \frac{V\rho_A g}{n_A} \quad \text{and} \quad 2\pi r\gamma_B = \frac{V\rho_B g}{n_B},$$

so that

$$\frac{\gamma_A}{\gamma_B} = \frac{\rho_A}{\rho_B} \cdot \frac{n_B}{n_A}$$

Thus, if the surface tension and the density of one of the liquids be known, n_A and n_B can be experimentally found out, the density be determined and the unknown surface tension can be evaluated. Generally, water is used as the reference liquid and the last equation modifies to

$$\frac{\gamma_X}{\gamma_{H_2O}} = \frac{\rho_X}{\rho_{H_2O}} \cdot \frac{n_{H_2O}}{n_X},$$

where X stands for the unknown liquid. The surface tension obtained in accordance of the aforesaid method is the *relative* surface tension, and not the absolute surface tension, since it is determined relative to the surface tension of the reference liquid.

Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.

2. Rinse the stalagmometer with distilled water. Then allow water to flow between two fixed marks, one above the bulb, and another below the bulb of the stalagmometer, and count the number of drops for water at least twice.
3. Remove any water from the stalagmometer and rinse it with a small amount of the supplied liquid SA and count the number of drops in the same manner as done in step 1.
4. Repeat step 2 using the supplied liquid SB.
5. Using a clean and dry specific gravity bottle determine the specific gravities of the supplied solutions SA and SB.
6. Calculate the relative surface tensions of SA and SB.

Results and Calculations:

4. Experimental temperature: _____ ℃
   Density of water at ___ ℃ = _____ g/ml.
   Surface tension of water at ___ ℃ = _____ dynes/cm.
5. Determination of the specific gravities:

Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
Empty		×	×	×
Water			1.0	
Liquid SA				
Liquid SB				

6. Determination of the relative surface tensions (γ_X):

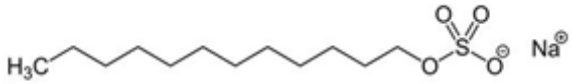
Substance	No. of Obs.	No. of drops	Means no. of drops	Relative surface tension (γ_X) (dynes/cm)
Water	1.			
	2.			
	3.			
Liquid SA	1.			
	2.			
	3.			
Liquid SB	1.			
	2.			
	3.			

Conclusion: The relative surface tensions of the supplied liquids SA and SB are determined to be and _____ dynes/cm at ____ °C.

Experiment 2: Determination of CMC from surface tension measurements.

Theory: Surfactants are water-soluble amphiphilic molecules that consist of a non-polar hydrophobic part (usually a hydrocarbon or fluorocarbon chain) and a polar hydrophilic part (head group). The hydrophilic head group can be non-ionic, anionic, cationic, or zwitterionic. The balance between hydrophobic and hydrophilic parts gives special properties to surfactants, e. g. high affinity to adsorb at interfaces and association in solution to form micelles. The concentration at which surfactants start to form micelles is called critical micelle concentration (CMC). Each surfactant has a characteristic CMC at a given temperature and salt concentration. The CMC of a surfactant can be obtained by different techniques, which in general are based on the measurement of a magnitude that shows an abrupt change at CMC. The surface tension at the air-water interface of a solution are examples of such magnitudes.

Sodium dodecyl sulphate (SDS), also called sodium lauryl sulphate, is an anionic surfactant commonly used in many cleaning and hygiene products.



Sodium dodecyl sulfate (SDS)

Here we implement the drop-weight (equivalent to the drop-counting) method to determine the surface tension of the supplied solution or liquid. The principle of the drop-weight method is based on the fact that when a liquid is allowed to flow through a capillary tube (thus ensuring almost streamline flow) and fall in drops from its end, the drop first remains sticking at the end of the capillary tube, but it falls down when its weight becomes just equal to the force of surface tension, acting on it. The weight w of a drop of liquid of density ρ and volume v is given by

$$w = v\rho g.$$

If the radius of the drop be r, and if γ be the surface tension acting on it, then the force due to surface tension is $2\pi r\gamma$, where $2\pi r$ is the circumference of the liquid drop. If there are n drops in a finite volume V, then the volume of a single drop, $v = V/n$. Therefore, under the condition of equilibrium

$$2\pi r\gamma = \frac{V\rho g}{n}$$

If two different liquids of densities ρ_A and ρ_B and surface tensions γ_A and $\gamma_B$are allowed to flow in equal volumes V through the same stalagmometer, and if n_A and n_B be the number of drops that make up for the volume V, then we must have

$$2\pi r\gamma_A = \frac{V\rho_A g}{n_A} \quad \text{and} \quad 2\pi r\gamma_B = \frac{V\rho_B g}{n_B},$$

so that

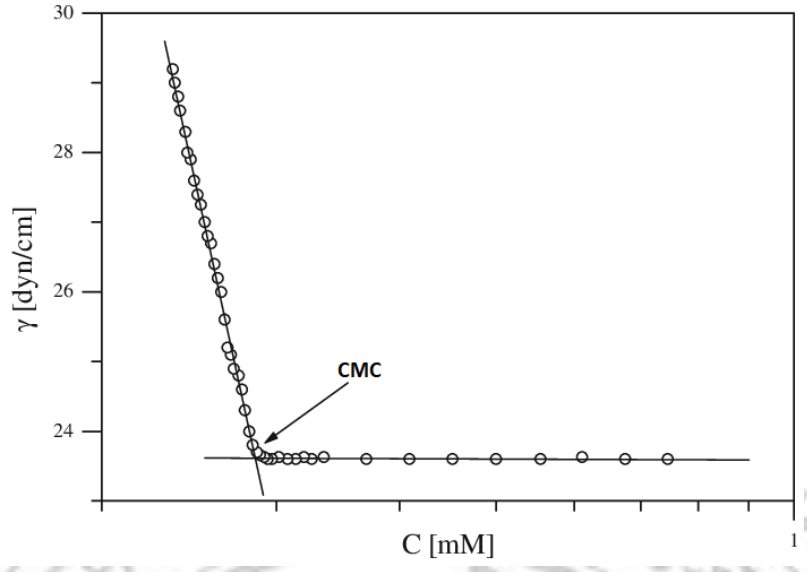
$$\frac{\gamma_A}{\gamma_B} = \frac{\rho_A}{\rho_B} \cdot \frac{n_B}{n_A}$$

Thus, if the surface tension and the density of one of the liquids be known, n_A and n_B can be experimentally found out, the density be determined and the unknown surface tension can be evaluated. Generally, water is used as the reference liquid and the last equation modifies to

$$\frac{\gamma_X}{\gamma_{H_2O}} = \frac{\rho_X}{\rho_{H_2O}} \cdot \frac{n_{H_2O}}{n_X},$$

where X stands for the unknown liquid. The surface tension obtained in accordance of the aforesaid method is the *relative* surface tension, and not the absolute surface tension, since it is determined relative to the surface tension of the reference liquid.

SDS solutions of different concentrations are prepared and the surface tensions are measured. From the plot of surface tension versus concentration, the CMC is determined at the experimental temperature.



Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.
2. Prepare a 1% (w/v) stock solution of SDS by dissolving 1 gm SDS in 100 ml distilled water in a 100 ml volumetric flask. Hence, the concentration is 1000 mg/100 ml = 10 mg/ml.
3. Take 8 nos. of clean 100 ml volumetric flasks to prepare the following solutions by pipetting out the 1% (w/v) stock solution of SDS (10.0 mg/ml) and making up the volume with distilled water.

Solution	Volume of 1% (w/v) stock solution of SDS (10 mg/ml) (ml)	Concentration (mg/ml)
1	0.5	0.05
2	1.0	0.10
3	2.0	0.20
4	5.0	0.50
5	10.0	1.00
6	20.0	2.00
7	40.0	4.00
8	80.0	8.00

4. Using a clean and dry specific gravity bottle to determine the specific gravities of all the solutions including water.
5. Rinse the stalagmometer with distilled water. Then allow water to flow between two fixed marks, one above the bulb, and another below the bulb of the stalagmometer, and count the number of drops for water at least twice.
6. Remove any water from the stalagmometer and rinse it with a small amount of solution 1 (of strength) and count the number of drops in the same manner as done in step 1.
7. Repeat step 5 using all the other solutions including the stock.
8. Calculate the relative surface tensions of all the solutions and plot a graph of surface tension against the concentration of the solution to determine the CMC.

Results and Calculations:

1. Experimental temperature: _____ ℃
   Density of water at ___ ℃ = _____ g/ml.
   Surface tension of water at ___ ℃ = _____ dynes/cm.
2. Determination of the specific gravities:

Substance	Wt. of sp. gr. bottle + substance (g)	Wt. of the substance w (g)	Specific gravity, $S = w/w_{H_2O}$	Density, ρ (g/ml) $S \times \rho_{H_2O}$
Empty		×	×	×
Water			1.0	
Solution 1				
Solution 2				
Solution 3				
Solution 4				
Solution 5				
Solution 6				
Solution 7				
Solution 8				
Stock				

3. Determination of the relative surface tensions (γ_X):

Substance	Obs.	No. of drops	Means no. of drops	Surface tension (γ_X) (dynes/cm)
Water	1.			
	2.			
	3.			
Solution 1	1.			
	2.			
	3.			
Solution 2	1.			
	2.			
	3.			
Solution 3	1.			
	2.			
	3.			
Solution 4	1.			
	2.			
	3.			
Solution 5	1.			
	2.			
	3.			
Solution 6	1.			
	2.			
	3.			
Solution 7	1.			
	2.			
	3.			
Solution 8	1.			
	2.			
	3.			
Stock	1.			
	2.			
	3.			

4. Table for graph

Substance	Concentration (mg/ml)	Surface tension (γ_X) (dynes/cm)
Water	0.0	
Solution 1	0.05	

Solution 2	0.10	
Solution 3	0.20	
Solution 4	0.50	
Solution 5	1.00	
Solution 6	2.00	
Solution 7	4.00	
Solution 8	8.00	
Stock	10.0	

5. From the graph of surface tension versus concentration, the break point is obtained at a concentration of _____mg/ml.

Conclusion: The CMC of SDS is _____mg/ml at ____°C.

Experiment 3: To test the validity of Lambert-Beer's law for $KMnO_4$ solution and determine the concentration of the supplied solution of $KMnO_4$ by using colorimeter/spectrophotometer.

Theory: Lambert-Beer's law states that when a monochromatic beam of light passes through a homogeneous solution of a substance which absorbs the radiation, the rate of decrease of intensity (I) of the radiation with the thickness (l) of the absorbing solution is proportional to the intensity of the incident radiation and to the concentration (c) of the light absorbing species in solution. This may be expressed as,

$$-dI/dl = kcl$$

where k is a proportionality constant. The above equation means that the intensity of the radiation (I) is reduced by an amount dI on passing through a length dl of the solution of concentration c (assumed to be uniform throughout the solution). Separating the variables, one obtains,

$$-dI/I = kcdl$$

Integrating the above equation with proper limits when, $l = 0, I = I_0$, the intensity of the incident light, and when, $l = l, I = I_t$, the intensity of the transmitted light, one obtains, $\ln(I_t/I_0) = -kcl$. Transforming the logarithmic term to base 10 (that is, $\log_{10}$) one obtains, $\log_{10}(I_t/I_0) = -(k/2.303)cl$

$$\therefore I_t = I_0 \times 10^{-\epsilon cl}, \text{where } \epsilon = k/2.303$$

The term optical density (OD) or absorbance (A) is defined as

$$OD = A = \log_{10}(I_t/I_0) = \epsilon cl$$

In the above equation ϵ is the molar extinction coefficient of the light absorbing species and l is the optical path-length in cm of the solution of concentration c moles lit^{-1}, through which the absorbing radiation passes, so that the unit of ϵ is mol^{-1} lit cm^{-1}. The last equation is the mathematical expression for the Lambert-Beer's law. The quantity ϵ is a characteristic of the light absorbing species (molecule or ion) and depends on the temperature and the wavelength of the radiation used. Thus, when a solution of an absorbing species is scanned through a range of wavelengths (λ), it is observed that a plot of ϵ versus λ (in nm) shows a characteristic maximum at a specific wavelength. The wavelength at which ϵ passes through a maximum is called the absorption maximum, λ_{max} of the species. When the solution of a substance obeys the Lambert-Beer's law, in a particular concentration range, the absorbance values of a series of such solutions of different concentrations at a fixed path-length (l) will show a linear dependence on the molar concentration (c). Thus, a plot of A versus c will be a straight line passing through the origin with a positive slope equal to ϵl. When $l = 1$ cm, the slope directly gives the value of ϵ. Such a plot is called a calibration curve and may be used to measure an unknown concentration of a solution of the same substance by measuring its absorbance at the same wavelength using the cell of the same path-length.

Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.

2. Prepare 100 ml standard oxalic acid solution of order (N/10).
3. Standardize the supplied ~(M/50) $KMnO_4$ solution with the standard (N/10) oxalic acid solution. [Procedure for standardization: Pipette out 10 ml of the standard (N/10) oxalic acid solution in a 250 ml conical flask and add 10 ml of the supplied 4(N) H_2SO_4 solution. Heat the solution to about 70–80 °C (and avoid boiling of the solution; oxalic acid decomposes on boiling), and titrate the hot solution with the supplied ~(M/50) $KMnO_4$ solution until the solution turns light pink in color. The color should be stable for approximately 30 seconds. Repeat the titration twice to have a concordant reading. Calculate the strength of the $KMnO_4$ solution. Convert the strength obtained in (N) to that in (M).]
4. From the standardized (M/50) $KMnO_4$ solution, prepare 100 ml of 10^{-3} (M) $KMnO_4$ solution in water by exact quantitative dilution in a 100 ml volumetric flask.
5. Take 9 test tubes (preferably of uniform diameter), label them from 1 – 9 and prepare the following sets of solutions

Test tube no.	1	2	3	4	5	6	7	8	9
Volume of 10^{-3} (M) $KMnO_4$ solution (ml)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Volume of water (ml)	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0

6. Set the wavelength of the spectrophotometer/colorimeter to 530 nm.
7. Set zero of the spectrophotometer/colorimeter. Set the percent transmittance $(\%T)$ of the spectrophotometer/colorimeter to 100 using water.
8. Measure the $\%T$ values of the solutions in test tubes marked 1 – 9, and also of the supplied unknown solution, each time rinsing the cell with the experimental solution.
9. Calculate the absorbance values using the formula $A = 2 - \log(\%T)$.
10. Plot A versus concentration and draw the best-fit line passing through the origin and the experimental points to verify the Lambert-Beer's law. Estimate the value of ϵ from the slope of this line for an optical path-length $l = 1$ cm. Find out the unknown concentration from this calibration curve.

Results and Calculations:

1. Experimental temperature: _____ °C
2. Weight of oxalic acid taken = _____ gm. Hence, the strength of oxalic acid solution is ……(N).
3. Standardization of the supplied $KMnO_4$ solution: Volume of oxalic acid pipetted out = 10 ml.

Obs.	Burette reading		Volume of $KMnO_4$ (ml)	Mean volume of $KMnO_4$ (ml)	Strength of $KMnO_4$
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

4. Quantitative dilution of the ……(N) = ……(M) $KMnO_4$ solution to 10^{-3} (M) $KMnO_4$ solution: Added ……ml of the ……(N) = ……(M) $KMnO_4$ solution in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water.
5. Preparation of sets:

Test tube no.	1	2	3	4	5	6	7	8	9
Volume of 10^{-3} (M) $KMnO_4$ solution (ml)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Volume of water (ml)	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0

6. The spectrophotometer was calibrated at $\lambda_{max} = 530$ nm.
7. Data of percent transmittance $(\%T)$:

Test tube no.	Concentration (M)	$\%T$	$A = 2 - \log_{10}(\%T)$
1	1.0×10^{-4}		
2	2.0×10^{-4}		

3	3.0×10^{-4}		
4	4.0×10^{-4}		
5	5.0×10^{-4}		
6	6.0×10^{-4}		
7	7.0×10^{-4}		
8	8.0×10^{-4}		
9	9.0×10^{-4}		
Unknown			

8. From the graph of A versus concentration:
   Slope, ϵ = …… mol^{-1} lit cm^{-1}.
   Concentration of the unknown solution = …… (M)

Conclusion: The molar extinction coefficient ϵ for $KMnO_4$ was found to be …… mol^{-1} lit cm^{-1}, and the concentration of the supplied unknown solution is …… (M) at _____ °C.

Experiment 4: To test the validity of Lambert-Beer's law for $K_2Cr_2O_7$ solution and determine the concentration of the supplied solution of $K_2Cr_2O_7$ by using colorimeter/spectrophotometer.

Theory: Lambert-Beer's law states that when a monochromatic beam of light passes through a homogeneous solution of a substance which absorbs the radiation, the rate of decrease of intensity (I) of the radiation with the thickness (l) of the absorbing solution is proportional to the intensity of the incident radiation and to the concentration (c) of the light absorbing species in solution. This may be expressed as,

$$-dI/dl = kcl$$

where k is a proportionality constant. The above equation means that the intensity of the radiation (I) is reduced by an amount dI on passing through a length dl of the solution of concentration c (assumed to be uniform throughout the solution). Separating the variables, one obtains,

$$-dI/I = kcdl$$

Integrating the above equation with proper limits when, $l = 0, I = I_0$, the intensity of the incident light, and when, $l = l, I = I_t$, the intensity of the transmitted light, one obtains,

$$\ln(I_t/I_0) = -kcl$$

Transforming the logarithmic term to base 10 (that is, $\log_{10}$) one obtains,

$$\log_{10}(I_t/I_0) = -(k/2.303)cl$$

$$\therefore I_t = I_0 \times 10^{-\epsilon cl}, \text{where } \epsilon = k/2.303$$

The term optical density (OD) or absorbance (A) is defined as

$$OD = A = \log_{10}(I_t/I_0) = \epsilon cl$$

In the above equation ϵ is the molar extinction coefficient of the light absorbing species and l is the optical path-length in cm of the solution of concentration c moles lit^{-1}, through which the absorbing radiation passes, so that the unit of ϵ is mol^{-1} lit cm^{-1}. The last equation is the mathematical expression for the Lambert-Beer's law.

The quantity ϵ is a characteristic of the light absorbing species (molecule or ion) and depends on the temperature and the wavelength of the radiation used. Thus, when a solution of an absorbing species is scanned through a range of wavelengths (λ), it is observed that a plot of ϵ versus λ (in nm) shows a characteristic maximum at a specific wavelength. The wavelength at which ϵ passes through a maximum is called the absorption maximum, λ_{max} of the species. When the solution of a substance obeys the Lambert-Beer's law, in a particular concentration range, the absorbance values of a series of such solutions of different concentrations at a fixed path-length (l) will show a linear dependence on the molar concentration (c). Thus, a plot of A versus c will be a straight line passing through the

origin with a positive slope equal to ϵl. When $l = 1$ cm, the slope directly gives the value of ϵ. Such a plot is called a calibration curve and may be used to measure an unknown concentration of a solution of the same substance by measuring its absorbance at the same wavelength using the cell of the same path-length.

Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.
2. Prepare 500 ml of ~1(N) H_2SO_4 solution in a stoppered bottle.
3. Prepare 100 ml of standard (M/50) $K_2Cr_2O_7$ solution in the ~1(N) H_2SO_4 in a volumetric flask by accurate weighing. From this standard solution, prepare 100 ml of 10^{-3} (M) $K_2Cr_2O_7$ solution in ~1(N) H_2SO_4 by exact dilution.
4. Take 9 test tubes (preferably of uniform diameter), label them from 1 – 9 and prepare the following sets of solutions

Test tube no.	1	2	3	4	5	6	7	8	9
Volume of 10^{-3} (M) $K_2Cr_2O_7$ solution (ml)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Volume of ~1(N) H_2SO_4 solution (ml)	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0

5. Set the wavelength of the spectrophotometer/colorimeter to 475 nm.
6. Set zero of the spectrophotometer/colorimeter. Set the percent transmittance $(\%T)$ of the spectrophotometer/colorimeter to 100 using ~1(N) H_2SO_4 solution.
7. Measure the $\%T$ values of the solutions in test tubes marked 1 – 9, and also of the supplied unknown solution, each time rinsing the cell with the experimental solution.
8. Calculate the absorbance values using the formula $A = 2 - \log(\%T)$.
9. Plot A versus concentration and draw the best-fit line passing through the origin and the experimental points to verify the Lambert-Beer's law. Estimate the value of ϵ from the slope of this line for an optical path-length $l = 1$ cm. Find out the unknown concentration from this calibration curve.

Results and Calculations:

1. Experimental temperature: _____ °C.
2. Weight of $K_2Cr_2O_7$ taken = _____ gm. Hence, the strength of $K_2Cr_2O_7$ solution is ……(N).
3. Quantitative dilution of the ……(N) = ……(M) $K_2Cr_2O_7$ solution to 10^{-3} (M) $K_2Cr_2O_7$ solution: Added ……ml of the ……(N) = ……(M) $K_2Cr_2O_7$ solution in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water.
4. Preparation of sets:

Test tube no.	1	2	3	4	5	6	7	8	9
Volume of 10^{-3} (M) $K_2Cr_2O_7$ solution (ml)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Volume of ~1(N) H_2SO_4 solution (ml)	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0

5. The spectrophotometer was calibrated at $\lambda_{max} = 475$ nm.
6. Data of percent transmittance $(\%T)$:

Test tube no.	Concentration (M)	$\%T$	$A = 2 - \log_{10}(\%T)$
1	1.0×10^{-4}		
2	2.0×10^{-4}		
3	3.0×10^{-4}		
4	4.0×10^{-4}		
5	5.0×10^{-4}		
6	6.0×10^{-4}		
7	7.0×10^{-4}		
8	8.0×10^{-4}		
9	9.0×10^{-4}		

Unknown			

7. From the graph of A versus concentration:
   Slope, ϵ = …… mol^{-1} lit cm^{-1}.
   Concentration of the unknown solution = …… (M)

Conclusion: The molar extinction coefficient ϵ for $K_2Cr_2O_7$ was found to be …… mol^{-1} lit cm^{-1}, and the concentration of the supplied unknown solution is …… (M) at _____ °C.

Experiment 5: To study the kinetics of the reaction between $K_2S_2O_8$ and KI by spectrophotometric method.

Theory: The overall reaction between $K_2S_2O_8$ and KI

$$K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$$

If a equivalent/liter of both the reactants, $K_2S_2O_8$ and KI are mixed, and if n be the overall order of the reaction, then the time t required for a definite fraction of the reactants o react will be inversely proportional to a^{n-1}, that is,

$$t \propto 1/a^{n-1}$$

Thus, if a_1 and a_2 equivalent/liter be the two starting concentrations of the two reactants and t_1 and t_2 be the times required for a definite fraction to react, then, from the above proportionality,

$$t_1/t_2 = (a_2/a_1)^{n-1}$$

On taking logarithm and rearranging, the last equation takes the following form that yields the order n of the reaction

$$n = 1 + \frac{\log(t_1/t_2)}{\log(a_2/a_1)}$$

Experimentally the value of n is found to be 2, that is, the reaction $K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$ is a second order reaction, being first order in $[K_2S_2O_8]$ and first order in $[KI]$ and the rate law may be expressed according to,

$$\text{Rate} = -\frac{d[K_2S_2O_8]}{dt} = k[K_2S_2O_8][KI]$$

where k is the second order rate constant in $\text{equivalent}^{-1} \cdot \text{liter} \cdot \text{second}^{-1}$.
If x equivalent/liter of $K_2S_2O_8$ has reacted in time t, then the above rate law takes the form

$$\frac{dx}{dt} = k(a-x)^2$$

Since at $t = 0$, $x = 0$, and at $t = t$, $x = x$, the above equation on integration takes the form

$$\frac{x}{a(a-x)} = kt$$

Since one of the products, I_2, is colored ($\lambda_{max} = 525$ nm) its absorbance A, at any instant of time t is proportional to the concentration x, provided Lambert-Beer's law I obeyed. The last equation is then transformed into

$$kt = \frac{1}{a} \cdot \frac{A_t}{A_\infty - A_t}$$

where A_t and A_∞ are the absorbance values at $t = t$ and $t = \infty$ respectively. On rearranging, we get

$$\frac{1}{A_t} = \frac{1}{A_\infty} + \frac{1}{akA_\infty}\frac{1}{t}$$

Thus, a plot of $1/A_t$ against $1/t$ will give a straight line with an intercept of $1/A_\infty$ and a slope equal to $1/akA_\infty$ from which the value of the rate constant, k, may be evaluated using the relation

$$k = (\text{intercept})/(a \times \text{slope})$$

Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.

2. Prepare 100 ml of a standard (N/10) $K_2Cr_2O_7$ and 100 ml of a standard KI (strength $>$ N/10) solutions by accurate weighing. Prepare 100 ml of a $K_2S_2O_8$ solution (strength $>$ N/10) and 250 ml of a ~1(N/10) $Na_2S_2O_3$ solution by weighing in a rough balance.
3. Standardize the $Na_2S_2O_3$ solution against the standard (N/10) $K_2Cr_2O_7$ solution following the usual procedure. [Pipette out an aliquot of 25 ml of the standard (N/10) $K_2Cr_2O_7$ solution in a 500 ml conical flask, add 25 ml of ~4(N) H_2SO_4 solution, and 2 g of $KI(s)$. Stopper the flask and keep it in the dark for about 3 minutes. Dilute with 150 ml distilled water to adjust the acidity to ~0.5(N) and titrate the liberated iodine with the thiosulphate solution till a straw yellow color appears. Add 2 ml of 1% starch indicator. The solution turns intense blue in color. Continue titration with the thiosulphate solution until the blue color just disappears and a light green color persists in the solution. Record the titer value.]
4. Take 10 ml of the prepared $K_2S_2O_8$ solution in a 500 ml conical flask, add 10 ml of 10% (w/v) KI solution and 2 ml of glacial acetic acid. Cover the conical flask with watch glass and keep the mixture in dark for 25 – 30 minutes. Add 80 ml distilled water and then titrate the liberated iodine with the standard ~(N/10) thiosulphate solution using starch indicator. Calculate the strength of the $K_2S_2O_8$ solution. Prepare an exact (N/10) $K_2S_2O_8$ solution by accurate dilution of this solution. [This process is time-consuming, and involves the use of expensive chemicals. Perform this standardization only once and with utmost care.]
5. Prepare an exact (N/10) KI solution by exact dilution of the prepared standard ($>$ N/10) solution.
6. Mix the $K_2S_2O_8$ and KI solutions as follows, one at a time, and note the time of half discharge of any one of the reactants in each case.

Set	(N/10) KI solution (ml)	(N/10) $K_2S_2O_8$ solution (ml)	Water (ml)
I	10	10	0
II	5	5	10

7. Record $\%T$ of these two sets of solutions at 525 nm wavelength at an interval of about 1 minute.
8. Plot A_t against t for the two sets. Find n from any set of values (t_1, A_1) and (t_2, A_2).
9. Plot $1/A_t$ against $1/t$ to determine k for both the sets and calculate the ratio of the rate constants.

Results and Calculations:

1. Experimental temperature: _____ °C.
2. Weight of $K_2Cr_2O_7$ taken = _____ gm. Hence, the strength of $K_2Cr_2O_7$ solution is ……(N).
3. Standardization of the $Na_2S_2O_3$ solution: Volume of $K_2Cr_2O_7$ solution pipetted out = 25 ml

Obs.	Burette reading		Volume of $Na_2S_2O_3$ (ml)	Mean volume of $Na_2S_2O_3$ (ml)	Strength of $Na_2S_2O_3$
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

4. Weight of KI taken = _____ gm. Hence, the strength of KI solution is ……(N).
5. Weight of $K_2S_2O_8$ taken in a rough balance = _____ gm.
6. Weight of $Na_2S_2O_3$ taken in a rough balance = _____ gm.
7. Standardization of the $K_2S_2O_8$ solution: Volume of $Na_2S_2O_3$ solution consumed = ……. ml. Hence, the strength of $K_2S_2O_8$ solution is …… (N).
8. Quantitative dilution of the $K_2S_2O_8$ solution: …… ml of the …… (N) $K_2S_2O_8$ solution was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water to prepare 100 ml exactly 0.1 (N) $K_2S_2O_8$ solution.
9. Quantitative dilution of the KI solution: …… ml of the …… (N) KI solution was transferred in a 100 ml volumetric flask using a burette and the volume was made up to the mark with distilled water to prepare 100 ml exactly 0.1 (N) KI solution.
10. Preparation of sets (one at a time for the kinetic study):

Set	(N/10) KI solution (ml)	(N/10) $K_2S_2O_8$ solution (ml)	Water (ml)

I	10	10	0
II	5	5	10

11.Kinetic data for Set-I: [10 ml (N/10) KI + 10 ml (N/10) $K_2S_2O_8$]

t (minutes)	$\%T$	$A_t = 2 - \log_{10}(\%T)$	$1/t$ (minute^{-1})	$1/A_t$
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				

12.Kinetic data for Set-II: [5 ml (N/10) KI + 5 ml (N/10) $K_2S_2O_8$ + 10 ml water]

t (minutes)	$\%T$	$A_t = 2 - \log_{10}(\%T)$	$1/t$ (minute^{-1})	$1/A_t$
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				

13.Plotted $1/A_t$ against $1/t$ to determine k_1 and k_2 for both the Sets I and II, respectively.

For Set-I, $k_1 = \text{intercept}/a \times \text{slope} =$ ..... lit equiv^{-1}minute^{-1}.

For Set-II, $k_1 = \text{intercept}/a \times \text{slope} =$ ..... lit equiv^{-1}minute^{-1}.

Ratio, $k_1/k_2 =$ ……

Conclusion: The rate constants were determined to be …… and …….. lit equiv^{-1}minute^{-1} for the two sets, and their ratio was found to be …….

Experiment 6: To determine the pK_{In} value of an acid-base indicator by spectrophotometric method.

Theory: Acid base indicators are weak (mostly organic) acids or bases having distinctly different colours in acidic and alkaline solutions, and by virtue of change of colour they indicate the end points of acid-base titrations. The ionization equilibrium of a weak acid indicator (HIn) may be represented according to,

$$\mathrm{HIn\ (acidic\ form)} \rightleftharpoons \mathrm{H^+ + In^-(alkaline\ form)}$$

for which the ionization constant, K_{In}, is given by

$$K_{\mathrm{In}} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]},$$

since, HIn and $\mathrm{In^-}$ have distinctly different colors depending upon their concentrations and pH of the solution, the ionization constant, K_{In}, of the indicator may be expressed according to,

$$K_{\mathrm{In}} = \frac{[\mathrm{H^+}][\mathrm{In^-}]_{\mathrm{colored}}}{[\mathrm{HIn}]_{\mathrm{colored}}}$$

$$\therefore pH = pK_{\mathrm{In}} + \log_{10}\frac{[\mathrm{In^-}]_{\mathrm{colored}}}{[\mathrm{HIn}]_{\mathrm{colored}}}$$

Thus, if a fixed amount of the indicator is placed in the same volume of a series of buffer solutions of different known pH values, the ratio $[\mathrm{In^-}]_{\mathrm{colored}}/[\mathrm{HIn}]_{\mathrm{colored}}$, will increase with the increase of pH. If the values of the ratio at different $pH$are determined by measuring the color intensity of the indicator solutions, then the pK_{In} value of the indicator can be found out if the pH of the buffer solutions are known.

If the alkaline form of the indicator ($\mathrm{In^-}$) absorbs at a selected wavelength and Beer's law is obeyed in the range of concentration of the indicator used, then the absorbance (A) of the indicator solution at a particular pH will be proportional to its concentration, provided the acid form (HIn) does not absorb at this wavelength.

$$A = \epsilon[\mathrm{In^-}]_{\mathrm{colored}}l.$$

In a strongly alkaline solution, HIn is practically absent, and the absorbance (A_{alkaline}) will correspond to the total concentration (T_{In}) of the indicator.

$$A_{\mathrm{alkaline}} = \epsilon T_{\mathrm{In}}l,$$

where ϵ is the molar extinction coefficient of $\mathrm{In^-}$ and l is the optical path length in cm. The mass balance equation of the indicator is,

$$T_{\mathrm{In}} = [\mathrm{HIn}]_{\mathrm{colored}} + [\mathrm{In^-}]_{\mathrm{colored}}$$

$$\therefore [\mathrm{HIn}]_{\mathrm{colored}} = T_{\mathrm{In}} - [\mathrm{In^-}]_{\mathrm{colored}}.$$

From the expressions for A and A_{alkaline},

$$[\mathrm{HIn}]_{\mathrm{colored}} = \frac{A_{\mathrm{alkaline}} - A}{\epsilon l}.$$

From the expression for A,

$$[\mathrm{In^-}]_{\mathrm{colored}} = \frac{A}{\epsilon l}$$

Substituting the values of $[\mathrm{HIn}]_{\mathrm{colored}}$ and $[\mathrm{In^-}]_{\mathrm{colored}}$ in the expression for pH,

$$pH = pK_{\mathrm{In}} + \log_{10}\left(\frac{A}{A_{\mathrm{alkaline}} - A}\right)$$

A and A_{alkaline} may be measured spectrophotometrically. Therefore, plotting $\log_{10}(A/(A_{\mathrm{alkaline}} - A))$ against pH of the buffer solutions, a straight line of slope unity will be obtained, of which the intercept on the pH axis will give the value of pK_{In}.

Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.
2. Prepare 100 ml standard oxalic acid solution of order (N/10).
3. Prepare 400 ml ~0.5 (N) (or slightly higher) solution of NaOH.
4. Prepare 400 ml ~0.5 (N) (or slightly higher) solution of AcOH.
5. Standardize the prepared ~0.5 (N) (or slightly higher) solution of NaOH against the standard oxalic acid solution using phenolphthalein as indicator.
6. Standardize the prepared ~0.5 (N) (or slightly higher) solution of AcOH against the standardized NaOH solution using phenolphthalein as indicator.
7. Quantitatively dilute the standardized NaOH solution to exactly 0.4 (N) in a 100 ml vol. flask.
8. Quantitatively dilute the standardized AcOH solution to exactly 0.4 (N) in a 100 ml vol. flask.
9. Take 12 test tubes (preferably of uniform diameter), label them from 1 – 12 and prepare the buffer solutions of the following compositions and mix uniformly in the first 9 test tubes.

Test Tube No.	Vol. of 0.4(N) AcOH (ml)	Vol. of 0.4(N) NaOH (ml)	Vol. of water (ml)	Total Vol. (ml)	pH (Experimental)
1	5.0	0.5	4.5	10.0	3.72
2	5.0	1.0	4.0	10.0	4.05
3	5.0	1.5	3.5	10.0	4.27
4	5.0	2.0	3.0	10.0	4.45
5	5.0	2.5	2.5	10.0	4.63
6	5.0	3.0	2.0	10.0	4.80
7	5.0	3.5	1.5	10.0	4.99
8	5.0	4.0	1.0	10.0	5.23
9	5.0	4.5	0.5	10.0	5.57

   In test tube numbers 10 – 12, take 2.5 ml of 0.4 (N) NaOH and add 7.5 ml of water.
10. Add a few (3-4) drops of the bromocresol green (BCG) indicator to test tube number 10.
11. Set the spectrophotometer wavelength to 570 nm. (This is the wavelength of maximum absorption, $\lambda_{\max}$ for BCG).
12. Measure the percent transmittance ($T_{\%}$) of the solution in test tube number 10. If the $T_{\%}$ value is less that 15%, take test tube number 11 and add fewer number of drops of the indicator to it and measure the $T_{\%}$ again. In this way by adjusting the number of drops of indicator, adjust the $T_{\%}$ of the alkaline form between 15% – 25% using test tube numbers 10 – 12 as required.
13. Add the same number of drops of BCG as adjusted in step 11 to each of the test tubes labeled 1 – 9 and measure their $T_{\%}$ values.
14. Calculate the absorbance values (A) for test tubes 1 – 9 and the A_{alkaline} value of the alkaline solution of the indicator (test tube 10 / 11 / 12) using the relation
$$A = 2 - \log_{10} T_{\%}$$
15. Plot $\log_{10}(A/(A_{\text{alkaline}} - A))$ against pH and draw the best straight line of unit slope with the experimental points being equidistant from the drawn line. Find pK_{In} from the intercept of the pH axis.

Results and Calculations:

1. Experimental temperature: _____ ℃
2. Preparation of 100 ml standard (N/10) oxalic acid solution: …… gm of oxalic acid was accurately weighed in an electronic balance and was subsequently dissolved in 100 ml distilled water to prepare a …… (N) oxalic acid solution.
3. Preparation of 400 ml approximately 0.5 (N) (or slightly higher) NaOH solution: ……. number of half beads of NaOH were dissolved in approximately 400 ml distilled water, followed by a thorough homogenization to prepare the desired NaOH solution.

4. Preparation of 400 ml approximately 0.5 (N) (or slightly higher) AcOH solution: ……. ml of glacial AcOH [17 (N)] was diluted to 400 ml to prepare the desired AcOH solution.
5. Standardization of the NaOH solution: Volume of oxalic acid solution pipetted out = …… ml

Obs.	Burette reading		Volume of NaOH (ml)	Mean volume of NaOH (ml)	Strength of NaOH
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

6. Standardization of the AcOH solution: Volume of AcOH solution pipetted out = …… ml

Obs.	Burette reading		Volume of NaOH (ml)	Mean volume of NaOH (ml)	Strength of AcOH
	Initial	Final			
1.	0.0				
2.	0.0				
3.	0.0				

7. Quantitative dilution of NaOH: ……. ml of ……. (N) NaOH solution was transferred using a burette into a 100 ml volumetric flask and the volume was made up to the mark with distilled water.
8. Quantitative dilution of AcOH: ……. ml of ……. (N) AcOH solution was transferred using a burette into a 100 ml volumetric flask and the volume was made up to the mark with distilled water.
9. Value of $T_{\%}$ for the alkaline solution (using test tube number 10 / 11/ 12) is …… for …… drops of BCG. Therefore, A_{alkaline} =……
10. Recording of $T_{\%}$ values for the buffer solutions and calculation of A values at $\lambda_{\max} = 570$ nm:

Test Tube No.	pH (Experimental)	$T_{\%}$	$A = 2 - \log_{10} T_{\%}$
1	3.72		
2	4.05		
3	4.27		
4	4.45		
5	4.63		
6	4.80		
7	4.99		
8	5.23		
9	5.57		

11. From the graph, the slope is …….. and the intercept (pK_{In}) is ……..

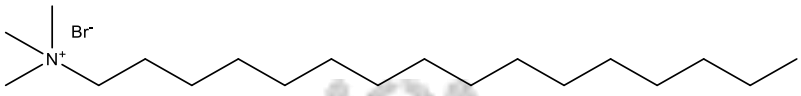
Conclusion: The pK_{In} for bromocresol green indicator is found to be …….. at …… °C.

Experiment 7: Spectrophotometric determination of CMC of cetyltrimethylammonium bromide (CTAB) using 2',7'-dichloro fluorescein (DCF) as indicator.

Theory: Surfactants are water-soluble amphiphilic molecules that consist of a non-polar hydrophobic part (usually a hydrocarbon or fluorocarbon chain) and a polar hydrophilic part (head group). The hydrophilic head group can be non-ionic, anionic, cationic, or zwitterionic. The balance between hydrophobic and hydrophilic parts gives special properties to surfactants, e. g. high affinity to adsorb at interfaces and association in solution to form micelles. The concentration at which surfactants start to form micelles is called critical micelle concentration (CMC). Each surfactant has a characteristic CMC at a given temperature and salt concentration. The CMC of a surfactant can be obtained by different techniques, which in general are based on the measurement of a magnitude that shows an abrupt

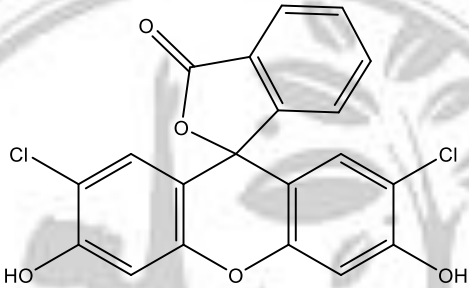
change at CMC. The surface tension at the air-water interface of a solution are examples of such magnitudes.

Cetyltrimethylammonium bromide (CTAB), molecular formula $C_{19}H_{42}N^{+}Br^{-}$ (molecular weight of 364.45), is a cationic surfactant, soluble in water and readily soluble in alcohol. CTAB is commonly used in the preparation and purification of genomic DNA from bacteria including DNA mini preps for sequencing. CTAB complexes with both polysaccharide and residual protein.



It is known that many dyes are stabilized in presence of micelles and exhibit marked spectral and colour changes. It is also known that the maximum colour changes occur when the charge on the surfactant micelle is opposite to that of the indicator ions.

2',7'-dichloro fluorescein (DCF), molecular weight 401.2, is an organic dye of the fluorescein family, being substituted at the 2' and 7' positions by chloride.



DCF has a λ_{max} of 515 nm in aqueous solutions. The $\%T$ of a series of mixtures of DCF-CTAB solutions, with DCF concentration held constant and CTAB concentrations being increases, can be measured. When both CTAB and DCF bear the same charge, the $\%T$ against increasing CTAB concentration falls rapidly reaching a minimum. As the CTAB concentration approaches the CMC (with the formation of micelles), DCF aggregates get dissociated from polymeric to the monomeric form and the solubilization of the dye will increase rapidly due to micellization. Hence, the intensity will reach its maximum at the CMC. With further increase in the CTAB concentration, however, colloidal particles are formed with consequent aggregation and adsorption of the DCF molecules resulting in an increase in the $\%T$. Therefore, the intensity maximum indicates the CMC of CTAB. Lambert-Beer's law can be suitably used to monitor this experiment. For a series of CTAB solutions (with varying CTAB concentrations and having a fixed number of drops of DCF indicator) the $\%T$ values are measured. The consequent absorbances (calculated by $A = 2 - \log_{10} \%T$) are plotted against CTAB concentrations and from the maximum in absorbance the CMC is determined.

Procedure: (*Please do not report in your laboratory notebook*)

1. Record the room temperature.
2. Prepare 100 ml 0.02 (M) (slightly higher) CTAB solution in distilled water, and dilute it quantitatively to an exact strength of 0.02 (M).
3. Prepare 50 ml of exactly 0.004% (w/v) DCF solution by accurate weighing in a chemical balance, and dilute it quantitatively to an exact strength of 0.0004% (w/v).
4. Prepare the following sets of CTAB solutions in 10 clean and dried test tube:

Test tube no.	1	2	3	4	5	6	7	8	9	10
Vol. of 0.02 (M) CTAB (ml)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Vol. of water (ml)	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0

5. Add two drops of the 0.0004% (w/v) DCF indicator solution to each of 10 test tubes and homogenize well.

6. Calibrate the spectrophotometer at a wavelength of 515 nm using water as the reference.
7. Read the $\%T$ values for the solutions in the 10 test tubes, convert the values to the corresponding absorbances and plot the absorbance values versus the concentration of CTAB. Determine the CMC from the maximum in absorbance.

Results and Calculations:

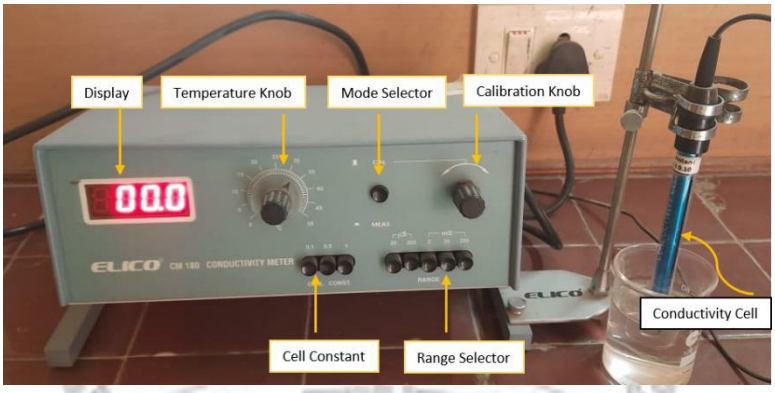
1. Experimental temperature: _____ ℃.
2. Preparation of 100 ml 0.02 (M) (slightly higher) CTAB solution: Weight of CTAB taken = ……. gm.
   ∴ The strength of CTAB = …… (M).
3. Quantitative dilution of the 0.02 (M) (slightly higher) CTAB solution of strength …… (M): Volume of CTAB transferred = ……. ml in a 100 ml volumetric flask using a burette. The rest of the volume was made up to the mark with distilled water.
4. Preparation of 50 ml of exactly 0.004% (w/v) DCF solution: Weight of DCF taken = ……. gm.
   ∴ The strength of DCF = …… %.
5. Quantitative dilution of the …… % DCF solution: Volume of DCF transferred = ……. ml in a 100 ml volumetric flask using a burette. The rest of the volume was made up to the mark with distilled water.
6. Data of percent transmittance $(\%T)$:

Test tube no.	CTAB Concentration (M)	$\%T$	$A = 2 - \log_{10}(\%T)$
1	2.0×10^{-3}		
2	4.0×10^{-3}		
3	6.0×10^{-3}		
4	8.0×10^{-3}		
5	10.0×10^{-3}		
6	12.0×10^{-3}		
7	14.0×10^{-3}		
8	16.0×10^{-3}		
9	18.0×10^{-3}		
10	20.0×10^{-3}		

   Two drops of DCF added to each test tube.
7. A graph of A versus CTAB concentration was plot and the value of CMC was determined to be …… (M).

Conclusion: The CMC of CTAB is spectrophotometrically found to be ……. (M) at …… °C.

USAGE INSTRUCTIONS FOR THE CONDUCTOMETER (MAKE: ELICO, SYSTRONICS)



Components of the Conductometer

(a) **Power switch:** It is located at the back of the instrument. When it is switched on, the display panel in the front glows.

(b) **Control Units of Conductometer:** All other controls are present on the front panel. A brief description of the various controls meant for conductivity measurement is tabulated below:

Temperature knob	With the help of this knob, the temperature can be set to values of 0 to 50 °C. Before any measurement, the temperature of measurement is set to the required value with this control.
Mode selector	This is a toggle switch present on the front panel of the instrument. It has the position marked CAL and READ. This is used to set the instrument either at the CAL (calibration) or READ(read) mode. When the toggle switch is in the depressed position, it is in the READ mode; otherwise, it is in the CAL mode.
CAL mode and the associated CAL knob	After selecting the CAL mode, the instrument is calibrated by rotating the CAL knob in clockwise or anticlockwise direction.
Cell constant	There are three keys for selecting the cell constant viz., $0.1, 0.5, 1$.
Range selector	There are five switches for selecting the range within which the conductance of the sample lies. These are marked $20\ \mu S, 200\ \mu S,$ $2\ mS, 20\ mS$ and $200\ mS$. When the range selector is at $20\ mS$, the conductometer reads between 2 and $20\ mS$.
Conductivity cell	It consists of two platinized (coated black) platinum electrodes with a cylindrical glass or plastic outer covering which is open at the bottom. This open end is dipped into the solution whose conductance is to be measured. From the top of the cell, emerge two leads which must be connected to the conductometer.

Operating instructions:

(a) Switch on the instrument and give it a warm up time of at least 15 minutes.

(b) Rinse the conductivity cell with the solution whose conductivity is to be measured.

(c) Dip the cell into the test solution, and set the READ/CAL key to the CAL position.

(d) The display must read 1000, irrespective of decimal. If it does not, then using the CAL knob set it to 1000.

(e) Set the temperature at the room temperature value using temperature knob; set the cell constant at 1.

(f) Dip the conductivity cell into a beaker containing the test solution taking care to dip the electrodes completely into the solution; shift the READ/CAL key to READ.

(h) Select any one range by pushing the range keys by trial and error so as to obtain a display with maximum decimal points.

(i) The display gives the specific conductance of the solution and since the cell constant is set to 1, it is also the observed conductance.

USAGE INSTRUCTIONS FOR THE pH METER (MAKE: ELICO, SYSTRONICS)

Components of the pH Meter

(a) **Power switch:** This switch is at the front of the instrument. When it is switched on, the display panel in the front glows.

(b) **Control Units of the pH Meter:** All other controls are present on the front panel. A brief description of the various controls meant for pH measurement is tabulated below:

Temperature knob	With the help of this knob, the temperature can be set to values of 0 to 50 °C. Before any measurement, the temperature of measurement is set to the required value with this control.
pH Calibration knob	This knob is used to calibrate the instrument with the given known pH solutions by rotating it clockwise/anticlockwise.
Standby/Read knob	While not in use, the instrument is kept at Standby mode. For readings, it is kept at Read position.
pH/mV knob	This knob is used to choose the display mode as pH or potential, as required.

Operating instructions:

A. Calibration:

The very first step towards measuring the pH of a solution is to calibrate the instrument. The steps of calibration are given below.

(a) Set the temperature to room temperature.

(b) Set the instrument to pH mode by pressing the pH/mV knob. Calibrate the pH-meter using buffer solutions of pH 4.01 (or any suitable buffer) ,7.0, and 9.2 (or any suitable buffer).

(c) Wash the electrode with water, wipe it gently with a soft tissue; rinse it with a buffer of pH 4.01.

(d) Dip it into a fresh buffer solution of pH 4.01.

(e) Swirl the solution and using the pH/mV push-button set the instrument to pH mode.

(f) Similarly using the standby/read push-button, set it to Read mode.

(g) Now note the pH from the display. If it is different from 4.01, then adjust the display to the desired value by rotating the CAL knob.

(h) Bring the instrument to the standby mode, remove the electrode from the buffer, wash it thoroughly with water, dab it gently with a soft tissue, rinse it with a buffer of pH 7.0 and calibrate with this buffer.

(i) Similarly calibrate the electrode with pH 9.2. Repeat the entire procedure of calibration with three buffer solutions at least three times or till the desired pH values are obtained for all the buffers used.

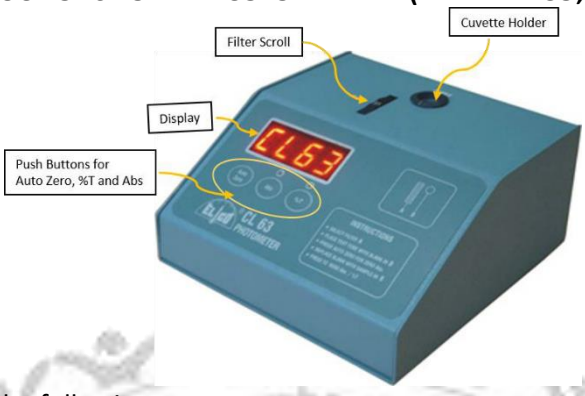
B. Measuring the pH of test solution

(a) Wash the electrode with water, wipe gently with soft tissue and rinse it with the test solution.

(b) Dip the electrode into another fresh aliquot of the test solution, set the instrument to pH or mV mode whichever is required and to Read mode by using standby/Read button.

(c) Read pH (or potential) from display panel. Set the instrument to standby mode. By selecting the mode to mV, the potential may be measured in the same manner as given above.

USAGE INSTRUCTIONS FOR THE COLORIMETER (MAKE: ELICO, SYSTRONICS)



A colorimeter consists of the following:
(a) **A display** which shows absorbance of a sample.
(b) **Filter scroll**: By rotating the scroll (wheel), the desired filter can be selected.
(c) **Cuvette holder (or cell compartment)**: to hold the sample.
(d) **Three push buttons:** (i) Auto Zero for setting absorbance to zero value, (ii) Abs for displaying absorbance, and (iii) %T for displaying the transmittance value.
(e) **Cuvettes or cells:** These are cylindrical in shape and are used to hold the sample. Pathlength is mostly of 1 cm.

Operating instructions:
Switch on the power of Colorimeter at least 15-20 minutes before start of the experiment.

A. Measuring the absorbance of blank:
(a) Take a clean, dry cuvette and fill it with the solvent (most of the time it is water) in which stock solution was prepared.
(b) Wipe off the surface of the cuvette with the help of tissue paper to get rid of solvent and fingerprints.
(c) Insert the cuvette in the sample holder aligning the white mark with the mark on the instrument.
(d) Choose the desired wavelength using Filter knob and set the absorbance to zero using the "Auto Zero" button; this means that the solvent gives 100% transmittance.
(e) Remove the cuvette and pour off the solvent.

B. Measurement of absorbance of test solution
(a) Now rinse and fill the cuvette with solution whose concentration is to be determined (stock solution), dry it from outside using tissue paper and insert it again.
(b) Check that the wavelength is set at the desired value and for which the autozero has been performed.
(c) Note the value of absorbance by pressing the "Abs" button. This will give the absorbance of substance at that particular wavelength.
(d) In case the solution is highly concentrated, absorbance goes out of range and the display does not show any reading, then the sample must be diluted to yield a value within the limits of the instrument.

USAGE INSTRUCTIONS FOR THE VISIBLE SPECTROPHOTOMETER (MAKE: SYSTRONICS MODEL 106)

A visible spectrophotometer (wavelength range of 340 nm – 960 nm) consists of the following:
(a) **A power switch** to set the instrument on/off.
(b) **A display** which shows absorbance/% transmittance of a sample.
(c) **Wavelength knob**: By rotating the knob, the wavelength (in multiples of 5 nm) can be selected.
(d) **Cuvette holders (or cell compartments)**: placed inside the flap, to hold the sample cuvette as well as the cuvette containing the reference liquid (usually the solvent in which the sample is prepared).
(e) **Filter scroll**: placed inside the flap, by rotating the scroll (wheel), the desired filter can be selected.
(f) **Push buttons:** (i) REF switch to perform the reference setting at the desired wavelength for the reference liquid, (ii) Abs/%T toggle switch to select between absorbance or % transmittance, (iii) CAL switch to calibrate the instrument and set either the %T to 100 or Abs to 0, and (iv) a Enter switch to record the Abs/%T value for the sample.
(g) **Cuvettes or cells:** These are glass vials of square cross-section and are used to hold the sample. Pathlength is mostly of 1 cm. Two opposite faces are transparent that allow the incident light to enter and the transmitted light to leave the sample.

Operating instructions:
Switch on the power of the spectrophotometer at least 15-20 minutes before start of the experiment.

A. Measuring the absorbance or % transmittance of blank:
(a) Set the desired wavelength using the wavelength knob, and set the filter to dark using the filter scroll. Set the instrument into the reference mode by pressing the REF switch. Press the Abs/%T toggle switch to select between absorbance or % transmittance.
(b) Take a clean, dry cuvette and fill it with the reference liquid/solvent (most of the time it is water) in which stock solution was prepared.
(b) Wipe off the surface of the cuvette with the help of tissue paper to get rid of the solvent and fingerprints.
(c) Insert the cuvette in the first sample holder aligning the two transparent faces along left and right.
(d) Press the REF switch again either to set the absorbance to 0, or to set the % transmittance 100 [depending on your choice of Abs/%T in step (a)].
(e) Remove the cuvette and set the filter to the appropriate range (in accordance with the selected wavelength) using the filter scroll.

B. Measurement of absorbance or % transmittance of test solution:
(a) Now rinse and fill the cuvette with the test solution whose absorbance or % transmittance has to be recorded, dry it from outside using tissue paper and insert it again.
(b) Press the Enter switch and note down the absorbance or % transmittance value from the display.
(c) Repeat steps (a) and (b) with the rest of the solutions.

USAGE INSTRUCTIONS FOR THE POTENTIOMETER (MAKE: EQUIPTRONICS MODEL EQ-601)

Components of the Potentiometer

(a) **Power switch:** It is located at the back of the instrument. When it is switched on, the display panel in the front glows.

(b) **Control Units of Potentiometer:** All other controls are present on the front panel. A brief description of the various controls meant for potential measurement is tabulated below:

Temperature probe	Connected to the point via a jack and a cable to the metallic probe, dipped in a beaker containing water at room temperature.
Jack point (red)	Point to connect the combined saturated glass calomel electrode.
Jack point (black)	Point to connect the test electrode (usually platinum/silver).
Mode selector switch (IN/OUT)	This is a toggle switch present on the front panel of the instrument. It has the position marked IN and OUT. This is used to set the instrument either at the calibration or read mode. When the toggle switch is in the OUT position, and if the instrument shows a value of 1.019, the instrument is already calibrated. When the toggle switch is in the IN position, it shows the value of the measured EMF in volts.
Adjustment screw	In case the toggle switch is in the OUT position, and the instrument does not show a value of 1.019, this screw is turned clockwise/anticlockwise to achieve this value.

Operating instructions:

(a) Switch on the instrument and give it a warm up time of at least 15 minutes.

(b) Dip the temperature probe into a beaker containing water at room temperature and connect the probe to the jack point at the back panel of the instrument.

(c) Prepare a saturated KCl solution (ensure that there is some undissolved KCl) in a 100 ml beaker and dip the combined glass calomel electrode into the solution.

(d) Connect the glass calomel electrode to the red jack point in the front panel of the instrument.

(e) Ensure that the instrument is calibrated properly, else do the needful as described above.

(f) Pipette out a definite volume of the test solution in another 100 ml beaker and dip the test electrode (usually platinum/silver) in it.

(g) Connect the test electrode to the black jack point in the front panel of the instrument.

(h) Insert the two ends of an appropriate salt-bridge into the two solutions (saturated KCl solution and the test solution).

(i) Homogenise by swirling the test solution carefully (avoid any spillage) and read the EMF value from the display.

USAGE INSTRUCTIONS FOR THE DIGITAL BALANCE (MAKE: METTLER TOLEDO XS-105-DU)

Operating instructions:

(a) Switch on the instrument and give it a warm up time of at least 15 minutes.

(b) Allow the display panel to show 0.0000; if it does not, press the TARE switch.

(c) In case step (b) fails, the instrument is possibly not levelled properly; use a spirit level at different locations of the base of the instrument to check. If the balance is not levelled properly, adjust the screws attached to the pedestals to level the instruments.

(d) Once the instrument shows 0.0000 in a stable manner, you are ready for weighing.

(e) Put a piece of weighing paper, and press TARE to set the zero.

(f) Weigh out the desired amount; while weighing is being carried out, all sorts of mechanical disturbances should be avoided; close the windows on the left and the right-hand sides to avoid such mechanical effects.

(g) Once weighing is over, shut down the balance, switch off the main and cover it with the jacket.

PART – II: LABORATORY MANUAL FOR INORGANIC CHEMISTRY

CONTENTS **PAGE**

1. Introduction:

Analytical chemistry studies and uses instruments and methods used to separate, identify, and quantify matter. In practice, separation, identification or quantification may constitute the entire analysis or be combined with another method. Separation isolates analytes. Qualitative analysis identifies analytes, while quantitative analysis determines the numerical amount or concentration. However, this lab manual includes the following topics:

- Inorganic Qualitative analysis
- Inorganic Quantitative analysis using-
  - ✓ Redox titration
  - ✓ Complexometric titration
  - ✓ Gravimetric Estimation
- Inorganic ions separation by paper chromatography
- Calorimetric Estimation of ions
- Inorganic Preparations

2. Qualitative analysis:

Qualitative analysis of inorganic salts means the identification of cations and anions present in the salt or a mixture of salts. Qualitative composition of materials can be determined by physical, physical-chemical and chemical methods of analysis. The aim of qualitative analysis is to establish chemical identity of the sample species, i.e. chemical elements, atom groups, ions or molecules, forming unknown substance or the mixture of substances.

Unknown material is converted to the compound with well-known characteristic properties. Such a conversion is called analytic reaction, while the substance inducing such a change is the reagent. It is carried out through the reactions which are easily perceptible to our senses such as sight and smell. Such reactions involve:

Table-1:

(a) Formation of a precipitate	(b) Change in colour	(c) Evolution of gas etc.
Systematic analysis of an inorganic salt involves the following steps: (i) Preliminary examination of solid salt and its solution. (ii) Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests. (iii) Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests. Preliminary examination of a salt often furnishes important information, which simplifies further course of analysis.		

First, we have to predict the colour of the given salts. Some compositions along with their respective colours are given bellow:

Table-2

Color	Example
BLACK	Ag_2S, CuO, CuS, HgS, PbS, FeS, MnO_2, CoO, CoS, NiS, NiO
GREEN	Cr_2O_3, all Cr^{3+} compounds, all Fe^{2+} (except black FeS), all Ni^{2+} (except NiO, NiS), $CuCO_3$, $Cu_3(BO_3)_2$, $CuCl_2$
RED	Pb_3O_4, Cu_2O, HgI_2, Fe_2O_3
ORANGE RED	All dichromate, Sb_2S_3.
BROWN	Fe_3O_4, Fe_2O_3, CdO
BLUE	Prussian Blue, anhydrous Co(II) Salts, Cu Compounds (except $CuCl_2$, Cu_2O, CuO, CuS)
YELLOW	AgI, Ag_3PO_4, CdS, As_2S_3, PbI_2, Fe^{3+} salts, all CrO_4^{2-} salts, $K_4[Fe(CN)_6]$
PINK	Cobalt salts except CoO, CoS, manganese salts except oxides, MnS, permanganates
COLOURLESS	All alkali and alkaline earth salts are colorless unless the anion is colored; most of the chlorides are colorless.

A. Physical Characteristics :

- Texture /Sample nature:
- Color:
- Solubility:

Cold water	Hot Water	Dilute HCl	Conc. HCl	Aqua regia	Cold water

B. Preliminary Tests For Basic radicals:

1. Dry Test Tube Heating

Experiment	Observation	Inference (Salts of)
Heating in a dry test tube	Yellow when hot and white when cold	$Zn(II), Sn(II)$
	Residue turns black	$Cu(II), Co(II), Ni(II), Mn(IV)$
	Yellowish Brown when hot, yellow when cold	$Pb(II)$
	Brown to black	Fe, Cr
	Green residue left	NO_3^-, NO_2^- of heavy metals
	Evolution of brown fumes with sublimate*	$As(III), Sb(III), NH^{4+}, Hg(II)$, etc.

* White/ black/yellow/etc.; to this sublimate add 1 drop conc. HCl and then pass H_2S gas; if yellow-orange color is developed, $Sb(III)$ may present, whereas a blackish colour indicates the presence of transition metals as well as $Bi(III)$.

2. Flame Tests

Element	Flame Color (Naked Eye)	Flame Color (Cobalt Blue Glass)
Sodium	Golden yellow	Nil
Potassium	Violet	Crimson
Calcium	Brick red	Light green
Strontium	Crimson	Purple
Barium	Yellowish-green (takes some time to appear)	Bluish-green
Copper	Bluish green	–
BO_3^{3-}/H_3BO_3	Yellowish-green (immediate response)	–

*Divided blue flame like a snake's tongue for tin.

3. Other experiments

Experiment	Observation	Inference (Salts of)
Borax bead test	Sky blue in Oxidizing Flame	Cu
	Deep blue in both oxidizing and reducing lames	Co
	N.B. Cu and Co containing samples exclusively response this test	
Oxidative fusion test	Green melt	Mn
	Yellow melt	Cr
Fluorescence test	Blue fluorescence	Sn

4. Wet test with different Extracts

HNO_3 extract:

Experiment	Observation	Inference (Salts of)
Extract + NH_4OH + AcOH + $K_4[Fe(CN)_6]$ soln.	Chocolate brown ppt.	$Cu(II)$
Extract + excess NH_4OH + DMG	Rose-Red ppt.	$Ni(II)$
Extract(cooled) + pinch of $NaBiO_3$	Pink colorization	$Mn(II)$
Extract + $K_4[Fe(CN)_6]$ soln.	Prussian blue color	$Fe(III)$
Extract + NH_4SCN soln.	Blood red color	

HCl extract:

Experiment	Observation	Inference (Salts of)
Extract (blue) diluted with water	Solution becomes pink	Co(II)
Dilute extract (blue) + $(NH_4)SCN$ + amyl alcohol + 2 drops conc. HCl	Blue (organic layer)	
Extract (blue) + large excess of water	Water turns milky	Sb(III)/Bi(III)*

*If upon addition of tartaric acid, the milky precipitate is dissolved, Sb is present.

NaOH extract:

Experiment	Observation	Inference (Salts of)
Extract (dil) + 2 drops dil. HCl + excess NH_4Cl	Gelatinous ppt.	Al(III)
1 ml extract (dil) + 1 drop Alizarin − S; AcOH added dropwise until the violet color just vanishes; 1 drop $AcOH$ added in excess.	Red coloration	
Extract (dil) + dil. AcOH + excess $K_4[Fe(CN)_6]$	Bluish white ppt	Zn(II)

C. Preliminary Tests For Acid radicals:

1. Dry test tube heating:

Experiment	Observation	Inference (Salts of)	Reaction(s)
Small amount of sample is heated in a test tube	Effervescence of colorless gas with pungent smell which turns blue litmus red, acidified $K_2Cr_2O_7$ paper green.	SO_3^{2-}	$MSO_3 \xrightarrow{Heat} MO + SO_2 \uparrow$ $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow \underset{Green}{Cr_2(SO_4)_3}$ Hydrated sulfides decompose on heating and gives H_2S.
	Colorless gas with a smell of rotten egg, turns moist $Pb(OAc)_2$ paper black.	S^{2-}	$Na_2S + 2H_2O \rightarrow 2NaOH + H_2S \uparrow$ $Pb(OAc)_2 + H_2S \rightarrow PbS \downarrow + 2AcOH$
	Reddish brown gas	NO_3^-/NO_2^-*	$MNO_2 \xrightarrow{Heat} MO + NO \uparrow$ $2NO + O_2 \rightarrow NO_2 \uparrow$ $2MNO_3 \xrightarrow{Heat} 2MO + 4NO_2 \uparrow + O_2$

*Some bromides decompose to give Br_2.

2. Test with dilute H_2SO_4:

Experiment	Observation	Inference (Salts of)	Reaction(s)
Take a pinch of the sample in a test tube, add 2-3 ml dilute H_2SO_4. If no reaction takes place in cold, warm a little. Test the gas evolved (if any).	Evolution of colorless gas having a smell of burnt Sulphur.	SO_3^{2-}	$MSO_3 + H_2SO_4 \rightarrow MSO_4 + H_2O + SO_2 \uparrow$
	Evolution of gas having rotten egg smell which blackens $Pb(OAc)_2$ paper black.	S^{2-}	$Pb(OAc)_2 + H_2S \rightarrow PbS \downarrow + 2AcOH$

3. Heating with concentrated H_2SO_4:

Experiment	Observation	Inference (Salts of)	Reaction(s)
A little sample is heated with conc. H_2SO_4.	The side wall of the test tube becomes oily and a water drop on a glass rod held on the mouth of the test tube turns opaque.	F^-	$MF + H_2SO_4 \xrightarrow{Heat} M_2SO_4 + HF$ $SiO_2 + HF \rightarrow SiF_4 + H_2O$ $3SiF_4 \underset{Green}{} + 3H_2O \rightarrow 2H_2SiF_6 + \underset{Green\ (waxy\ liq)}{H_2SiO_3}$ $Na_2B_4O_7 + 6MF_2 \rightarrow Na_2SO_4 + 6MSO_4 + 7H_2O + \underset{burns\ with\ green\ flame}{BF_3\uparrow}$
	A paste is made by mixing a little amount of sample, borax and conc. H_2SO_4. The paste is then taken in on the tip of a platinum loop and held at the flame.		
	A brown gas evolved on strong heating & the color intensified on addition of Cu turnings.	Br^-	$MBr + H_2SO_4 \rightarrow HBr + MHSO_4$
	A violet vapor evolved.	I^-, NO_3^-, NO_2^-*	$MNO_2 + H_2SO_4 \xrightarrow{Heat} M_2SO_4 + HNO_2$ $2HNO_2 \xrightarrow{Heat} 2HNO_3 + NO\uparrow$ $2NO + O_2 \rightarrow \underset{Brown}{NO_2}\uparrow$
	A brown gas evolved on strong heating and the color intensified on addition of Cu turnings.		

*Sometimes Br^- may also respond.

4. Other tests with concentrated H_2SO_4:

Experiment	Observation	Inference (Salts of)	Reaction(s)
A little amount of sample is treated with 2-3 ml H_2SO_4 and 5ml of MeOH and heated. The issuing gas is then burnt.	Green flame	BO_3^{3-} or H_3BO_3	$M_3BO_3 \xrightarrow{H^+} M_2SO_4 + H_3BO_3$ $H_3BO_3 + MeOH \rightarrow \underset{Brown}{B(OCH_3)_3}\uparrow$
A little amount of sample is treated 5ml of MeOH (without H_2SO_4) and heated. The issuing gas is then burnt.	Green flame	H_3BO_3	$H_3BO_3 + MeOH \rightarrow \underset{Brown}{B(OCH_3)_3}\uparrow$

5. Chromyl chloride test:

Experiment	Observation	Inference (Salts of)	Reaction(s)
The mixture of sample and $K_2Cr_2O_7$ is treated with conc. H_2SO_4 and heated.	Reddish-yellow gas evolved.	Cl^-	$MCl_2 + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2M(HSO_4)_2 + 2KHSO_4 + 3H_2O + \underset{\text{Red}}{2CrO_2Cl_2}$
The evolved red gas is passed into $NaOH$ solution.	The $NaOH$ solution turns yellow.		$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{Yellow}}{Na_2CrO_4} + 2NaCl + 2H_2O$
The yellow solution is acidified with $AcOH$ and $Pb(OAc)_2$ solution is added.	Yellow precipitate		$Na_2CrO_4 + Pb(OAc)_2 \rightarrow \underset{\text{Yellow}}{PbCrO_4} + 2NaOAc$
A mixture of sample and MnO_2 is treated with H_2SO_4 and heated.	Evolution of a pungent smelling gas, forms dense white fumes with NH_4OH moistened glass rod	Cl^-	$2MX + 3H_2SO_4 + MnO_2 \rightarrow 2MHSO_4 + MnSO_4 + 2H_2O + X_2 \uparrow$
	Reddish brown gas turns CS_2 layer yellow.	Br^-	
	Violet vapor turns CS_2 layer violet.	I^-	

6. Other dry tests:

Experiment	Observation	Inference (Salts of)	Reaction(s)
Sample is dissolved in conc. HNO_3 and $(NH_4)_2MoO_4$ is added in cold condition.	A canary yellow precipitate which disappears on heating with NH_4OAc.	PO_4^{3-}, AsO_4^{3-}	$Na_2HPO_4 + HNO_3 + (NH_4)_2MoO_4 \rightarrow \underset{\substack{\text{Canary yellow}\\ \text{Ammonium phosphomolybdate}}}{(NH_4)_3[PMo_{12}O_{40}]}$
	A canary yellow precipitate, which turns white on heating with NH_4OAc.		$Na_2AsO_4 + HNO_3 + (NH_4)_2MoO_4 \rightarrow \underset{\substack{\text{Canary yellow}\\ \text{Ammonium arsenomolybdate}}}{(NH_4)_3[AsMo_{12}O_{40}]}$
Iodine-azide test	Effervescence of N_2 gas	$S^{2-}, SCN^-, S_2O_3^{2-}$	

D. Wet test for acid radicals:

(a) Preparation of Na_2CO_3 extract:

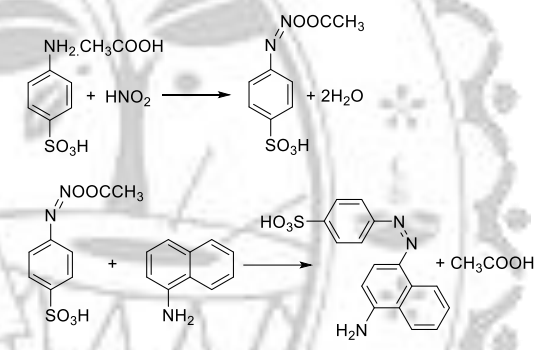
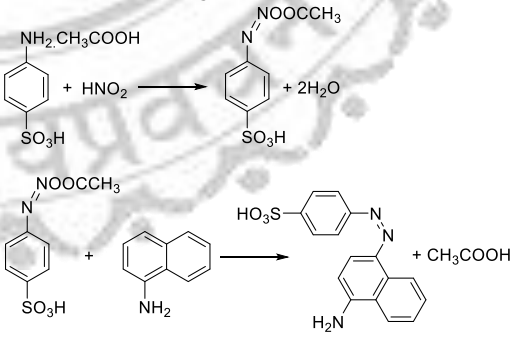
About 1g of sample is taken in a 250 ml beaker and about 2 gm of Na_2CO_3 is added along with 2-3 beads of solid $NaOH$ and then add about 50 ml of distilled water within the mixture. The solution is digested for 15 minutes. Then after filtration, the filtrate is used as Na_2CO_3 extract. During the preparation of Na_2CO_3 extract a double decomposition reaction takes place with the bivalent and trivalent metallic salts.

$$MA_n + Na_2CO_3 \rightarrow M_nCO_3 + 2Na_nA\ (A = S^{2-}, SO_4^{2-}, Cl^-, Br^-, etc.)(n = 1,2, \dots)$$

In the extract, the acid radicals of the salts get combined with Na^+ to form salts which are water soluble. If the supplied salts are water insoluble only then such extract should be prepared.

Experiment	Observation	Inference (Salts of)	Reaction(s)
1. To a part of the extract 2-3 ml of concentrated HNO_3 is added to remove CO_2 and then $AgNO_3$ solution was added.	Curdy white precipitate soluble in dilute NH_4OH solution	Cl^-	$Na_2CO_3 + 2HNO_3 \xrightarrow{\text{Heat}} 2NaNO_3 + CO_2 + H_2O$ $NaCl + AgNO_3 = \underset{\text{White}}{AgCl}\downarrow + NaNO_3$ $AgCl + 2NH_4OH = \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl}\downarrow$
	Very little yellow precipitate, soluble in strong NH_4OH solution.	Br^-	$NaBr + AgNO_3 = \underset{\text{Yellow}}{AgBr}\downarrow + NaNO_3$ $AgBr + 2NH_4OH \underset{\text{conc.}}{=} \underset{\text{Soluble}}{[Ag(NH_3)_2]Br}\downarrow$
	Yellow precipitate, insoluble in strong NH_4OH.	I^-	$NaI + AgNO_3 = \underset{\text{Yellow}}{AgI}\downarrow + NaNO_3$
2. (a) A part of the extract is acidified with dilute HCl and then 2-3 ml CCl_4/CS_2 is added. By adding 3-4 ml of Cl_2-water, the solution is shaken.	CCl_4 layer turns violet	I^-	$2NaI + Cl_2 = 2NaCl + \underset{\text{Violet}}{I_2}$
2. (b) Excess Cl_2-water is added with it.	CCl_4 layer turns red brown.*	Br^-	$2NaBr + Cl_2 = 2NaCl + \underset{\text{Red}}{Br_2}$
3. To a part of the extract 2-3 drops of sodium nitroprusside solution is added.	Violet colour appears.	S^{2-}	$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow \underset{\text{Violet}}{Na_4[Fe(CN)_5NOS]}$
4. A part of the extract is acidified with conc. HNO_3 and boiled to remove CO_2. $BaCl_2$ solution is added to it. Excess HCl is added to it.	White ppt appears which is insoluble in excess HCl.	SO_4^{2-}	$Na_2SO_4 + BaCl_2 \rightarrow \underset{\text{White (insoluble in excess HCl)}}{BaSO_4}\downarrow + 2NaCl$
	White ppt appears which is soluble in excess HCl. On addition of Cl_2-water precipitate reappears.	SO_3^{2-}	$Na_2SO_3 + BaCl_2 \rightarrow \underset{\text{White (soluble in excess HCl)}}{BaSO_3}\downarrow + 2NaCl$ $BaSO_3 + Cl_2 + H_2O \xrightarrow{[O]} BaSO_4 + 2HCl$

*[In case of mixture I^- and Br^-, with excess Cl_2-water violet colour disappears to give a yellowish-brown colour.]

Experiment	Observation	Inference (Salts of)	Reaction(s)
5. To apart of the extract 2-3 drops of very dilute $FeCl_3$ Solution is added	Transient violet color.	$S_2O_3^{2-}$	$Na_2S_2O_3 + FeCl_3 \rightarrow Na[Fe(S_2O_3)_2]$ (Violet, transient) $Na_2S_2O_3 + 2FeCl_3 \rightarrow Na_2S_4O_6 + 2FeCl_2 + 2NaCl$ At first violet color is formed which dissociates readily to tetrathionate and colorless $FeCl_2$.
6. Extract + $Pb(OAc)_2$ soln.	Yellow precipitate	CrO_4^{2-}	$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow PbCrO_4 \downarrow + 2CH_3COONa$ (Yellow)
7. A part of the solution is acidified with AcOH and heated to boil off CO_2. To this little thiourea 2-3 drops of dil. HCl and 2-3 drops of $FeCl_3$ solution is added.	Red coloration appears.	SCN^-	$(NH_2)_2CS + HNO_2 \rightarrow N_2 + HSCN + 2H_2O$ $Fe^{3+} + SCN^- \rightarrow [Fe(SCN)]^{2+}$ (Red)
8. A part of the extract is neutralized or acidified with dil. AcOH on a spot plate and mix it with a drop of the sulphanilic acid reagent, followed by a drop of the α-naphthylamine reagent (cold condition).	Red colored azo dye	NO_2^-	
9. A part of the extract is acidified with dil. AcOH on a spot plate and treated with Zn dust. Mix with it a drop of the sulphanilic acid reagent, followed by a drop of the α-naphthylamine reagent.(cold condition)	Red colored azo dye	NO_3^-	$NaNO_3 + AcOH \rightarrow HNO_3 + NaOAc$ $Zn + 2CH_3COOH \rightarrow 2[H] + (CH_3COO)_2Zn$ $NaNO_3 + 2[H\} \rightarrow NaNO_2 + H_2O$ 
10. To a part of the extract 2-3 drops of $FeCl_3$ solution is added.	Prussian blue color/ppt	$[Fe(CN)_6]^{4-}$	$Na_4[Fe(CN)_6] + FeCl_3 \rightarrow NaFe[Fe(CN)_6] \downarrow + 3NaCl$ $3NaFe[Fe(CN)_6] + FeCl_3 \rightarrow Fe_4[Fe(CN)_6] \downarrow + 3NaCl$ (Prussian blue)

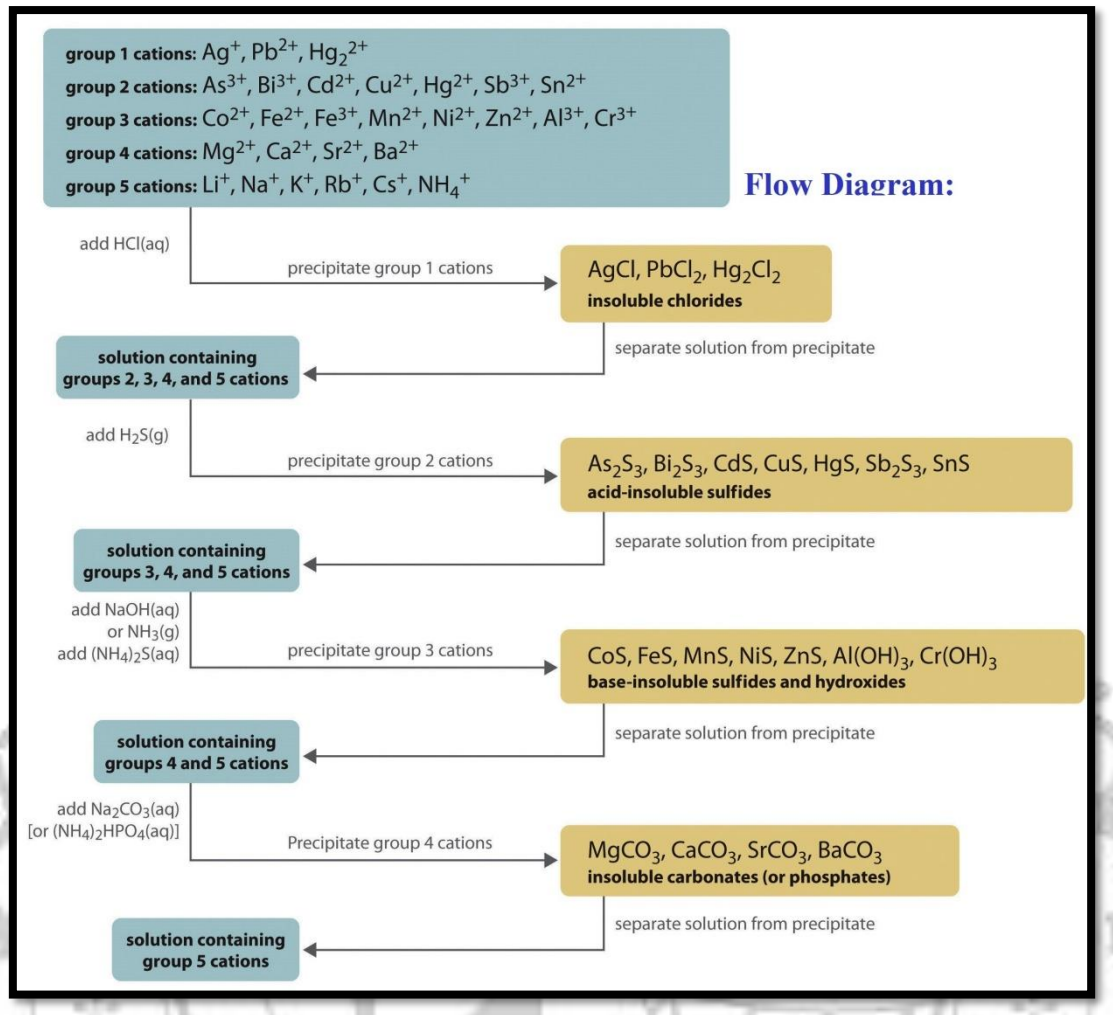
Experiment	Observation	Inference (Salts of)	Reaction(s)
11. To a part of the extract freshly prepared $FeSO_4$ solution (1 ml) is added.	Prussian blue color/ppt	$[Fe(CN)_6]^{3-}$	$Na_3[Fe(CN)_6] + FeSO_4 \rightarrow NaFe[Fe(CN)_6] \downarrow + Na_2SO_4$ $NaFe[Fe(CN)_6] + FeSO_4 \rightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} \downarrow + Na_2SO_4$
12. Extract is acidified with conc. HNO_3 and heated to boil off CO_2; added 2 ml $(NH_4)_2MoO_4$ solution. (No heating)	A canary yellow ppt	PO_4^{3-}	$HPO_4^{2-} + 3NH_4^+ + 12MoO_4^{2-} + 23H^+ \rightarrow (NH_4)_3[P(Mo_{12}O_{40})] + 12H_2O$
13. A part of the extract is acidified with conc. HNO_3 and heated to boil off CO_2 followed by the addition of 2 ml $(NH_4)_2MoO_4$ soln.; soln. is boiled. (Canary yellow ppt + NH_4OAc soln.; heated to boiling; The soln. is cooled)	Yellow ppt is soluble in dil. NH_3/dil. HNO_3	PO_4^{3-}	$Na_3AsO_4 + HNO_3 \rightarrow Na_2HAsO_4 + NaNO_3$ $Na_2HAsO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 = (NH_4)_3[AsMo_{12}O_{40}] + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$ The ppt in fact contains the *tris* molybdate ion $Mo_3O_{10}^{2-}$, each replacing one O in AsO_4^{3-}, that is, $[As(Mo_3O_{10})_4]^{3-}$. $(NH_4)_3[As(Mo_3O_{10})_4] + CH_3COONH_4 \rightarrow [AsO_4]^{3-} + [MoO_4]^{2-} + [Mo_7O_{20}]^{2-}$ $[AsO_4]^{3-} \xrightarrow{H^+} \underset{\text{White}}{H_3AsO_4 \cdot H_2O}$
	Ppt dissolved to form a clear solution.	AsO_4^{3-}	
Test for PO_4^{3-} in presence of AsO_4^{3-}			
14. A part of the extract is treated with conc. HNO_3, tartaric acid and $(NH_4)_2MoO_4$,ammonium molybdate.	Yellow ppt	PO_4^{3-}	Reactions as above
	No yellow ppt	AsO_4^{3-}	
15. Extract is acidified with dil. HNO_3, boiled off CO_2, $AgNO_3$ added.	A ppt either white/light yellow, insoluble in HNO_3.	$Cl^-, Br^-, I^-, BrO_3^-, IO_3^-$	Reactions as above
	A white ppt turned yellow on treatment with Na_2SO_3 and dil. H_2SO_4.	IO_3^-	Reactions as above

E. Group Separations for cations:

The qualitative analysis of cations depends on the solubility products of the ions. The cations get precipitated on the optimum needed concentration and easily detected. Before that, solutions preparation have to be done systematically with proper ways.

10 ml aq solution + few ml dil HCl or allow to cool the hot HCl solution of the sample. Filter & wash the ppt with cold water.	
Gr. I present/Absent	Taking the filtrate, Adjust acidity to 0.3 N. Warm. Pass H_2S till ppt. completed. Filter.

<table>
<tr><td></td><td colspan="3"></td></tr>
<tr><td>Residue:
Present/Absent
Gr-II (A+B)</td><td colspan="3">Filtrate: H_2S was boiled off, few drops of conc. HNO_3 was added and boiled again (*mainly to oxidise Fe^{2+} to Fe^{3+}), then interfering acids radicals (F^-, BO_3^{-3} and PO_4^{-3}) was/were removed in the following ways (if they present):
a) Borate/Fluoride was/were removed by complete evaporation of the solution 3-4 times with cons. HCl.
b) Phosphate was removed by $FeCl_3$-acetate buffer method which is given the in the separate table.
[if there is no such interfering acids like F^-, BO_3^{-3} and PO_4^{-3}, then the test solution was directly used for respective group separation normally.]
After removal of the given interfering acid radical, the test solution in dil. HCl was warmed with appropriate amount of solid NH_4Cl, then NH_4OH solution was added until the smell of NH_3 persists, shaken and filtered:</td></tr>
<tr><td></td><td>Residue:
Present/Absent
Gr-III (A)</td><td colspan="2">Filtrate: Appropriate amount of NH_4OH solution was added, heated to boiling, H_2S was passed completely, filtered the solution:</td></tr>
<tr><td></td><td>Residue:
Present/Absent
Gr-III (B)</td><td colspan="2">Filtrate: The volume of the solution was reduced to ¼ by evaporation, then NH_4OH solution & saturated $(NH_4)_2CO_3$ solution was added, warmed & filtered:</td></tr>
<tr><td></td><td></td><td>Residue:
Present/Absent
Gr-IV [mention colour of ppt.]</td><td>Filtrate:
Gr.-V</td></tr>
</table>



Separation of ppt of Group IIA & IIB	
Transfer the ppt in a 100 mL beaker. Add ammonium sulphide solution & 2 N KOH. Warm. Filter. Wash the ppt with water.	
Residue: Group IIA (PbS/ HgS/Bi_2S_3/ CuS/ CdS)	Filtrate: Group IIB sulphides of As, Sb, Sn. Dilute with water. Add dil HCl. Filter. Reject filtrate. Yellow or Orange ppt—As_2S_3/Sb_2S_3/SnS.
Treatment of ppt of GROUP IIA	
Transfer the ppt in a 100 mL beaker. Boil with 1:3 HNO_3.	

<table>
<tr><td rowspan="3">Residue: HgS- Black. Insoluble in conc HCl Hg^{2+} confirmed.</td><td colspan="3">Filtrate: Take little filtrate adds dil H_2SO_4—White ppt. Pb^{2+} confirm.
If Pb^{2+} present, add dil H_2SO_4 and EtOH to the main filtrate and filter.
If Pb^{2+} absent, don't add those.</td></tr>
<tr><td rowspan="2">Residue: $PbSO_4$ White Dissolve the ppt in saturated NH4-acetate solution and add K_2CrO_4. Yellow ppt. Pb^{2+} Confirmed.</td><td colspan="2">Filtrate: Boil off EtOH if added & add excess NH_4OH, filter.</td></tr>
<tr><td>Residue: White Wash with water & dissolve the ppt in dil HCl :
To a part of the solution, add freshly prepared Na- stannite solution— Black ppt— Bi^{3+} confirmed.</td><td>Filtrate: If filtrate is colourless, Cu^{2+} is absent. Then pass H_2S—a yellow ppt—Cd^{2+} confirms.
If filtrate is Blue:
Add dil AcOH + $K_4[Fe(CN)6]^{-}$ Chocolate coloured ppt— Cu^{2+} confirmed.</td></tr>
</table>

<table>
<tr><th colspan="2">Treatment of the ppt of Group IIB</th></tr>
<tr><td colspan="2">Transfer the ppt of the group IIB in 100 mL beaker. Boil with conc. HCl. Filter. Wash with water.</td></tr>
<tr><td>Residue: Insoluble Yellow ppt –As(III) confirmed as As_2S_3.</td><td>Filtrate:
• add NH_4OH + Oxalic Acid(s). Boil. Pass H_2S—Orange ppt confirms Sb^{2+}
• Partially neutralize the other part with NH4OH. Add few pieces of iron wire. Boil for few minutes. Filter. To the filtrate add $HgCl_2$ solution— white/grey ppt.- Sn^{2+} confirmed.</td></tr>
</table>

<table>
<tr><th>Phosphate separation Table</th></tr>
<tr><td>Boil off H_2S from the filtrate of GROUP II, boil with 1mL conc. HNO_3 to oxidize Fe^{2+} (if present) to Fe^{3+} .
Main bulk of solution + NH4Cl(s) + NH4OH until smell of NH_3. Dissolve the ppt in dil HCl. Add NH4OH dropwise until ppt appears. Add an equal vol of buffer solution prepared by mixing 4 mL glacial AcOH + 36 mL sat. Ammonium acetate solution (pH= 4.6). Add freshly prepared $FeCl_3$</td></tr>
</table>

solution drop wise with constant stirring until the solution turns raw tea colour. Dilute the mixture with about 10 mL of water. Boil for 2 minuits. Filter in hot & wash the residue with little hot water.

Analysis of group IIIA.	
Transfer the ppt into 100 mL beaker, add dil NaOH solution & about 5 mL of "10 volume" H_2O_2, boil till effervescence ceases. Cool. Filter.	
Residue: Dissolve it in dil HNO3 & divide it into 2 parts: • Add $K_4[Fe(CN)_6]$ solution – a deep blue ppt—Fe^{3+} confirmed.	Filtrate: Divide in 2 parts. • Add solid NH4Cl to a part of the solution and boil.—A white gelatinous ppt confirmed Al(III). • If the solution is yellow, Cr(VI) is present. Acidify the solution with AcOH + Pb-Acetate—Yellow ppt—Cr(III).

Analysis of group IIIB		
Transfer the ppt in a 100 mL beaker & treat it with 1 (N) HCl. Filtered the solution:		
Residue: CoS & NiS. Confirmed Co(II) by Borax Bead Test. Dissolve the ppt in dil HCl. Divide into 2 parts : • Add NH4OH until ammoniacal. Add few drops DMG—Rose red ppt—Ni(II) present. • Add NH_4SCN solution + few mL amyl alcohol + NH_4HF_2 & shake alcohol layer turns blue—Co(II).	Filtrate: Boil off H_2S. Add excess of NaOH solution, warm and filter	
	Residue: Dissolve the ppt in nitric acid and then add a pinch of solid $NaBiO_3$. Solution changes into pink indicates the presence of Mn(II).	Filtrate: Acidify a part of the filtrate with dil AcOH. Pass H_2S. White ppt—Zn(II).

Analysis of group IV		
Dissolve the ppt in hot 2 (N) AcOH. Add K_2CrO_4 solution to the main bulk till the solution is coloured slightly yellow. Warm the solution and solution and then filtered:		
Residue: Yellow $BaCrO_4$ Confirm Ba^{2+} by flame test (apple green).	Filtrate: Add a little of Na_2CO_3, white ppt indicates presence of $SrCO_3$ and/or $CaCO_3$. Wash the ppt with hot water & dissolve it in dil AcOH. Add a saturated solution of $(NH_4)_2SO_4$. Heat to boiling. Filter.	
	Residue: White $SrSO_4$. Perform flame test after reducing it on the tip of the Bunsen burner. Crimson red flame – Sr^{2+} .	Filtrate: Render a part of it ammoniacal. Add ammonium oxalate

		solution, heat in a water bath. White ppt – Ca^{2+} (brick red flame also confirm it).

*Group-V solution was divided into two parts, one part (small volume) was evaporated to dryness to perform flame test for Na^+ (golden-yellow flame) & K^+ (*Crimson through double blue glass).
Taking the final filtrate from group-V, following wet can also be performed to identify the Gr-V cation.

i) Zinc Uranyl Acetate test for Na^+ (insoluble Yellow ppt.)
ii) Sodium Cobaltinitrite test for K^+
iii) Titan Yellow test for Mg^{2+} (should not present PO_4^{-3})
iv) When disodium hydrogen phosphate solution is added and the inner walls of the test tube are scratched with a glass rod, if a white crystalline precipitate of is formed indicates the presence of Mg (II) ions.
[N.B. NH_4^+ may be confirmed by soda-lime test (dry test tube heating) but **not from the group-V solution.]**

F. INSOLUBLE TREATMENT:

INSOLUBLE COMPOUNDS	COLOUR
Al_2O_3, SnO_2, $CaSO_4$ (sparingly soluble), $BaSO_4$, $SrSO_4$, CaF_2, $PbSO_4$	White
Cr_2O_3	Green
Fe_2O_3	Dark red/ Brown
$PbCrO_4$	Brown/ Yellow

✓ $BaSO_4$, $SrSO_4$, $CaSO_4$:

The insoluble residue is fused with Na_2CO_3 and NaOH on a mica foil. The mass is kept in the liquid state for 5 minutes. The fused mass is cooled and extracted with hot water and filtered

<table>
<tr><td colspan="2">Residue:
The residue is boiled with dil AcOH. Filtered if any un-dissolved residue is left</td><td rowspan="2">Filtrate:
Filtrate is acidified with dil. HCl (blue litmus red) and CO_2 is boiled off. $BaCl_2$ or $Ba(NO_3)_2$ solution is added to the solution
→ White heavy precipitate insoluble in dil. HCl
→SO_4^{2-}

[With this filtrate test for insoluble SnO_2 may also be performed]</td></tr>
<tr><td>Filtrate: Filtrate is divided into three part
1. The 1st part of the filtrate is treated with $K_2Cr_2O_4$ →Yellow ($BaCrO_4$) →Ba^{2+}
2. The 2nd part of the filtrate is treated with CH_3COONH_4 and $(NH_4)_2SO_4$ and heated →White ($SrSO_4$) →Sr^{2+}
3. The 3rd part of the filtrate is treated with CH_3COONH_4 and ammonium oxalate and boiled</td><td>Residue:
Rejected</td></tr>
</table>

→White (CaC_2O_4) →Ca^{2+}		

** $CaSO_4$ is sparingly soluble.

- ✓ **$PbSO_4$:**

The white insoluble residue is boiled with a concentrated solution of CH_3COONH_4 and a few drops of AcOH. Filter if any undissolved residue is left.

Filtrate:	Residue:
Filtrate is divided into 3 parts 1. To the 1st part KI solution is added. → a yellow precipitate is soluble on boiling and reappears on cooling → Pb^{2+} confirmed. 2. To the 2nd part K_2CrO_4 solution is added → a yellow precipitate $PbCrO_4$ →Pb^{2+} confirmed 3. To the 3rd part few drops of conc. HNO_3 is added, warmed and then $BaNO_3$ is added →A white precipitate ($BaSO_4$) → SO_4^{2-}	Rejected

- ✓ **Al_2O_3**: White

The insoluble residue was fused with Na_2CO_3 and NaOH on a mica foil. The mass is kept in the liquid state for 5 minutes. The fused mass is cooled and extracted with hot water and filtered.

Filtrate:	Residue:
Solid NH4Cl is added to the filtrate and boiled → A white gelatinous white precipitate is formed →Al^{3+}	Rejected

- ✓ **Cr_2O_3** and **Fe_2O_3:**

The insoluble residue is fused with Na_2CO_3 and KNO_3 on a mica foil. The mass is kept in the liquid state for 5 minutes. The fused mass is cooled and extracted with hot water and filtered.

Filtrate:	Residue:
The filtrate is acidified with AcOH and then $Pb(CH_3COOH)_2$ solution is added. → A yellow precipitate ($PbCrO_4$) → Cr^{3+}	Brown [Fe(OH)3] The residue is heated with concentrated HCl and then few drops of $K_4Fe(CN)_6$ solution is added. →Deep Blue precipitation. →Fe^{3+}

The ignite Fe_2O_3 is insoluble but the supplied sample is generally not the ignited one so we have some of the Fe_2O_3 dissolved in concentrated HCl and thus it is obtained in HCl extract

- ✓ **CaF_2**:

Experiments	Observations	Inferences

1. The insoluble residue is warmed with concentrated H_2SO_4 in a test tube. A drop of water on a glass rod is held at the mouth of the test tube.	Oily appearance on the inner wall of the test tube. The water drop becomes waxy.	F^-
2. Flame test was performed with the sample.	Transient crimson red coloured flame appeared. (after a long time)	Ca^{2+}

The insoluble residue was fused with Na_2CO_3 and NaOH on a mica foil. The mass is kept in the liquid state for 5 minutes. The fused mass is cooled and extracted with hot water and filtered

Residue: The residue is boiled with dil AcOH. Filtered if any undissolved residue is left		Filtrate: Rejected.
Filtrate: The filtrate is treated with CH_3COONH_4 and ammonium oxalate and boiled → White (CaC_2O_4) → Ca^{2+}	**Residue:** Rejected	

- ✓ **$PbCrO_4$:**

The brown substance is fused with a (or, two) piece of NaOH on a mica foil. The mass is dissolved in water by boiling. The solution is cooled and filtered if any un-dissolved residue is left.

Filtrate: Acidified with excess HCl and filtered		Residue: Rejected
Residue (white): Residue is boiled with water and KI solution is added → a yellow precipitate dissolves on heating with water and reappears on cooling as golden yellow silky needles → Pb^{2+}	Filtrate (yellow): It is neutralized with NH_4OH, acidified with dil. AcOH and a solution of $Pb(CH_3COOH)_2$ is added. → A yellow precipitate is formed → CrO_4^{2-}	

- ✓ **SnO_2:**

The insoluble residue is fused with Na_2CO_3 and NaOH on a mica foil. The mass is kept in the liquid state for 5 minutes. The fused mass is cooled and extracted with hot water and filtered

Residue: Reject [With this residue test for insoluble **$BaSO_4$, $SrSO_4$, $CaSO_4$** may also be performed]	**Filtrate:** (Na2SnO3) is acidified with conc. HCl, boiled and H2S gas is passed →Yellow Precipitation (SnS_2) → Sn^{4+}

❖ Estimation of Fe^{3+} and Cu^{2+} in a supplied solution by Redox titration

Theory

A **redox titration** is a type of titration based on a redox reaction between the analyte and titrant. It may involve the use of a redox indicator and/or a potentiometer.

As an oxidant, **dichromate** has some advantages over permanganate, but, as it is less powerful, its use is much more limited. It is obtainable in a state of high purity and can be used as a primary standard. Solutions of dichromate in water are stable indefinitely. The half reaction for the dichromate system is:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad E° = 1.33$ V

The most important application of dichromate is in its reaction with iron(II) in which it is often preferred to permanganate. The relevant half reaction is : $Fe^{2+} \rightarrow Fe^{3+} + e^- \quad E° = -0.77$ V and the total reaction is:

$$\mathbf{Cr_2O_7^{2-} + 6\,Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6\,Fe^{3+} + 7H_2O} \quad E° = 0.56 \text{ V}$$

Unlike permanganate, dichromate titrations require an indicator. There are three indicators that may be used for the titration of Fe^{2+} with $K_2Cr_2O_7$. These are diphenylamine, diphenylbenzidine and diphenylamine sulfonate. The colour change for all three indicators is green to violet and the standard electrode potentials are all ca 0.78 V. According to Kolthoff and Sandell, this should lie between the electrode potentials of the two reduction reactions. This not being the case, phosphoric acid is added to reduce the electrode potential for the $Fe^{3+} \rightarrow Fe^{2+}$ reaction by stabilising the ferric ion.

The **iodometric titration** is a general method to determine the concentration of an oxidising agent in solution. In an **iodometric titration**, a starch solution is used as an indicator since it can absorb the I_2 that is released.

Iodometric determination of copper is based on the oxidation of iodides to iodine by copper (II) ions, which get reduced to Cu^+. Comparison of standard potentials for both half reactions (Cu^2+/Cu^+ E^0=0.15 V, I_2/I^- E^0=0.54 V) suggests that it is iodine that should be acting as oxidizer. However, that's not the case, as copper (I) iodide CuI is very weakly soluble ($K_{sp} = 10^{-12}$). That means concentration of Cu^+ in the solution is very low and the standard potential of the half reaction Cu^{2+}/Cu^+ in the presence of iodides is much higher (around 0.88 V).In effect reaction taking place in the solution is:

$$\mathbf{2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2}$$

Here produced equivalent amount of iodine can be titrated with thiosulfate solution.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

1. Preparation of stock solution:

Carefully open the cap of the sample bottle and then transfer the supplied solution quantitatively into a 250 ml volumetric flask. Finally make the volume up to mark using distilled water.

(Heading with preparation method)

2. Preparation of 250 ml standard (N/20) $K_2Cr_2O_7$ solution:

Weigh out accurately **0.6125** gm $K_2Cr_2O_7$ and dissolve it by distilled water in 250 ml volumetric flask. (Table must)

3. Standardization of given thiosulphate solution:

Pipette out 25 ml of std. (N/20) $K_2Cr_2O_7$ solution into a 500 ml conical flask. Add **25 ml 4(N) H_2SO_4, 2gm of KI**, close the mouth of the flask with a watch glass and keep the flask with its contents in **dark for 2-3 minutes.** Wash the watch glass and inner sides of the flask with distilled water. **Dilute to 200 ml** with distilled water and titrate immediately with **$Na_2S_2O_3$** solution running from a burette until the ***brown colour* fades to *straw yellow***. Add **2 ml of freshly prepared starch solution** and **shake to obtain deep blue colour**. Then titrate the thio-solution very carefully until the colour changes to sharply from

intense ***blue to bright green*** **with one drop.** Record the titre value of thio-solution and calculate its strength.

4. **Estimation of Cu^{2+} ion by Iodometric method**:

Procedure: Pipette out **25 ml of stock solution** into a 500 ml conical flask, neutralize with **(1:1) NH_3** to obtain a permanent turbidity (**avoid excess NH_3**) and dissolve the same by adding about **2 gm of NH_4HF_2**. Add **2 gm of KI**, **diluted to 100 ml** with distilled water and titrate immediately with standard thio-sulphate solution until **brown colour fades to straw yellow. Add 2 ml of starch solution** and continue the titration until **colour fades to pale blue**. Then add **1 gm of solid NH_4SCN**, shake and titrate immediately **until pale blue colour just disappears to give a milky white solution**. Note the titre value and calculate the amount of Cu^{2+} ion present in the supplied solution in 250 ml.

[1000 ml 1(N) $Na_2S_2O_3$ equivalent to 63.55 gm of Cu^{2+}]

5. **Dichrometry titration of Fe^{3+} ion:**

Pipette out 25 ml of stock solution into a 500 ml beaker. Dilute the solution to about 100 ml with distilled water, add ~1 gm NH_4Cl and warm a little. Add dropwise 1:1 aqueous ammonia solution with constant stirring till the smell of ammonia persists. Allow the precipitate to settle for 5 min. And then filter through what man 41 paper. Wash the precipitate twice with washing liquid, 1% aqueous NH_4Cl solution containing few drops of NH_3. Dissolve the precipitate in minimum volume of hot (1:1) HCl and hot distilled water, successively. Reprecipitate Fe^{3+} ion quantitatively with (1:1) aqueous ammonia as mentioned earlier and allow to stand for settling down the precipitate. Refilter the precipitate through the same filter paper and wash as before. Dissolve the precipitate in 50 ml of (1:1) hot HCl and finally wash with hot distilled water until the filter paper becomes colourless. Heat the solution to about 80^0 C then add small pieces of AR grade Al-foil stepwise to reduce Fe(III) quantitatively to Fe(II), swirl the solution till all the Al-foil gets dissolved to room temperature and diluted to 150 ml with distilled water. Then add 5 ml syrupy H_3PO_4 or ~ 2 gm NH_4HF_2 and 5-6 drops of BaDS indicator & 1 ml conc. HCl and titrate the solution with the standard (N/20) $K_2Cr_2O_7$ solution to a reddish-violet end point. Record the titre value to calculate the total amount of iron present supplied sample.

(1000 ml 1(N) $K_2Cr_2O_7$ solution equivalent to 55.85 of Fe^{3+})

❖ **Determine separately at the amount in grams of Fe and Cr present in the supplied mixture of Fe(III) and $Cr_2O_7^{2-}$**

- **Procedure**

1. Prepare a 250 ml standard N/20 $K_2Cr_2O_7$ and get your weighing data signed by the examiner.
2. Standardization of Mohr's salt: Take 25 ml of the supplied Mohr salt N/20 in a 250 ml conical flux. Add 50 ml 2N H_2SO_4, 5 ml syrupy H_3PO_4 and 5-6 drops of BDS indicator and titrate with standard N/20 $K_2Cr_2O_7$ as usual. Find out the strength of Mohr salt solution.
3. Transfer the supplied solution, marked by ''I'' quantitatively by washing with water to a 250 ml volumetric flux, make up the volume with water and shake to obtain a uniform solution (stock solution).
4. **Estimation of Cr:** Pipette out 25 ml aliquot from the stock solution in a 500 ml conical flux. Add successively 25 ml of 4N H_2SO_4, 50 ml Standard Mohr's salt by means of pipette, 5 ml syrupy H_3PO_4 and 5-6 drops of BDS indicator. Titrate the resulting mixture with standard $K_2Cr_2O_7$ as usual. Record the titre and find out the amount in grams of Cr present n the supplied sample.
5. **Estimation of Fe**: Pipette out 25 ml aliquot from the stock solution in a 500 ml beaker, dilute with 50 ml water and add 1:1 NH_4OH drop wise with stirring until a permanent strong smell of NH_3 appears. Digest the mixture without boiling on a low flame for 3-4 mints. Filter through Whatman 41 filter paper and wash the beaker and the precipitate with 0.1 % NH_4Cl containing 5-6 drops NH_3. Place the original beaker under the funnel, dissolve the $Fe(OH)_3$ in minimum volume of hot 6N HCL (alternately equal volume of conc. HCl and hot water) and wash the filter paper with 100 ml of hot distilled water in portions and collect all the Fe(III) and the washing Together. Do not discard the filter paper. Re-precipitate $Fe(OH)_3$ from the Fe(III) obtained above by NH_4OH as usual. Filter through the same filter paper and wash the ppt as

same above. Dissolve the ppt and wash the filter paper free from any yellow stain by using alternatively a total of 30 ml conc. HCl and 30 ml of hot water. Collect all the solution in the same beaker. Introduce a few pieces of Al foils, heated with constant stirring until reduction Fe(III) is complete with the formation of A clear colourless solution. Add about 120 ml water and cool it rapidly under tap water to room temperature. Add 5 ml syrupy H_3PO_4, 5-6 drops of BDS indicator and titrate the mixture with the standard $K_2Cr_2O_7$ as usual. Record the titre. Find out the total Fe contain of the supplied solution.

❖ Determination of Available Chlorine in Bleaching Powder

Aim

To determine the available chlorine in the given sample of bleaching powder by the iodometric method.

Principle:

Bleaching powder is commonly used as a disinfectant. The chlorine present in the bleaching powder gets reduced with time. So, to find the exact quantity of bleaching powder required, the amount of available chlorine in the sample must be found out.
Chlorine will liberate free iodine from potassium iodide solution when its pH is 8 or less. The iodine liberated, which is equivalent to the amount of active chlorine, is titrated with standard sodium thiosulphate solution using starch as indicator.

Apparatus

Mortar and pestle
Volumetric flask
Burette
Pipette
Erlenmeyer flask.

Reagents

Concentrated glacial acetic acid
Standard sodium thiosulphate solution (0.025N)
Potassium iodide
Starch indicator
Iodine solution (0.025 N).

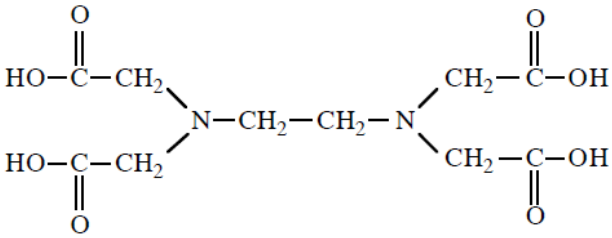
Procedure:

Dissolve 1g bleaching powder in 1 litre of distilled water in a volumetric flask, and stopper the container. (This can be done by first making a paste of the bleaching powder with mortar and pestle.) Place 5 mL acetic acid in an Erlenmeyer flask and add about 1g potassium iodide crystals. Pour 25 mL of bleaching powder solution prepared above and mix with a stirring rod. Titrate with 0.025 N sodium thiosulphate solution until a pale yellow colour is obtained. (Deep yellow changes to pale yellow.) Add 1mL of starch solution and titrate until the blue colour disappears. Note down the volume of sodium thiosulphate solution added (V_1). Take a volume of distilled water corresponding to the sample used. Add 5 mL acetic acid, 1g potassium iodide and 1 mL starch solution. If blue colour occurs, titrate with 0.025 N sodium thiosulphate solution until the blue colour disappears. Record the volume of sodium thiosulphate solution added. If no blue colour occurs, titrate with 0.025 N iodine solution until a blue colour appears. Note down the volume of iodine. Then, titrate with 0.025 N sodium thiosulphate solution till the blue colour disappears. Record the volume of sodium thiosulphate solution added. Note down the difference between the volume of iodine solution and sodium thiosulphate.

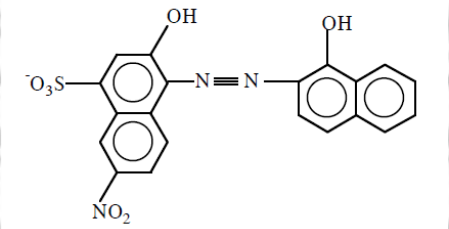
❖ Determination of calcium by Standardized EDTA Solution

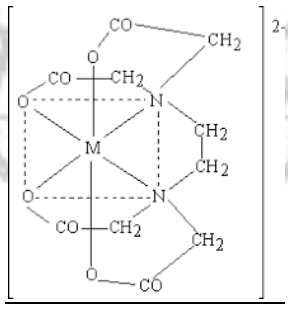
Introduction:

Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. **Complexometric** titrations are particularly useful for the **determination** of a mixture of different metal ions in solution. The classic method of determining calcium titration with a standardized solution of ethylenediaminetetraacetic acid (EDTA). EDTA has the structure shown below. Instead of repeatedly drawing this structure or writing out the chemical formula, the EDTA molecule is represented as "H4Y". Each acid hydrogen on EDTA can be removed, producing H_3Y^{-1}, H_2Y^{-2}, HY^{-3}, and Y^{-4} ions. The disodium dihydrate of EDTA, $Na_2H_2Y \bullet 2H_2O$ is commonly used to prepare standard EDTA solutions.



such a high purity that solutions need not be standardized for routine work. Primary standard calcium carbonate can be used to standardize EDTA solutions. Of the various EDTA species, only the Y^{4-}-ion(the completely deprotonated anion of EDTA) forms a 1:1 complex with metal ions. To increase the fraction of Y^{4-}-, the pH needs to be increased to 10 in this experiment. The endpoint of an EDTA titration is determined with a metallochromic indicator. These indicators are complexing agents that change color when combined with metal ions. A variety of indicators can be used for EDTA titrations. In this experiment, we will use Eriochrome black T (EBT) indicator, having the structure shown below:





his indicator (shown as H_2In^- in the equations below) changes from blue to red when combined with a metal ion, forming a complex ion:

EDTA is a stronger complexing agent than the indicator, and displaces the indicator from the metal ion allowing the indicator to return (through shades of violet) to a pure blue color, indicating the end of the reaction.

$$M^{2+} + H_2In^- + 2H_2O \text{ <--> } MIn^- + 2H_3O^+$$
blue red

$$MIn^- + Y^{4-} \text{ <--> } MY^{2-} + H_2In^-$$
red blue

Calcium ion (Ca^{+2}) does not form a stable red complex with the EBT indicator; therefore the direct titration of $Ca^{2+}$by EDTA may not cause a sharp color change of EBT indicator at the end point. The magnesium complex with EBT is stable and the K_f of $Mg^{2+}$with EDTA is lower than the K_f of $Ca^{2+}$with EDTA. Thus, a displacement titration of Ca^{2+} by the mixture of Mg^{2+} and EDTA will help to determine the end point with the following mechanism:

$$CaIn^- + MgY^{2-} \text{ <--> } CaY^{2-} + MgIn^-$$

To accomplish this displacement titration, a small amount of Mg^{2+}will be mixed with the EDTA solution. The $EDTA^-$ -Mg mixture will titrate the unknown Ca^{2+}solution. At the end point, Mg^{2+}will be released from the EBT indicator and complexed with EDTA, causing the color change from red to blue.
Solutions need for such experiments:

Solutions prepared by the student	Solutions provided by the instructor
0.01M disodium EDTA with $MgCl_2$ (standardized by student)	12M Hydrochloric acid
Standard Ca^{2+} solution	8.5M NH_3-NH_4Cl Buffer
Solution of egg shells	Eriochrome black T indicator

- ✓ **Experimental Procedure**:

Preparation and standardization of 0.01 M EDTA solution.
1.Using the top loading balance, weigh between 3.6 and 3.7 grams of disodium EDTA dihydrate into a clean 1 L plastic bottle. EDTA will leach metal ions from soft glass containers, and should never be stored in glass containers. Add 1 L of de-ionized water .EDTA dissolves SLOWLY. Shaking or stirring the solution vigorously speeds the dissolution process. Nevertheless, even under these conditions EDTA dissolves SLOWLY. It is strongly recommended that the EDTA solution be prepared several hours or even the day before you plan on using it. Before use, check the solution to make sure all of the solid has dissolved.

3. Experimental Procedure Preparation and standardization of 0.01 M EDTA solution.1.Using the top loading balance, weigh between 3.6 and 3.7 grams of disodium EDTA dihydrate into a clean 1 L plastic bottle. EDTA will leach metal ions from soft glass containers, and should never be stored in glass containers. Add 1 L of de-ionized water. EDTA dissolves SLOWLY. Shaking or stirring the solution vigorously speeds the dissolution process. Nevertheless, even under these conditions EDTA dissolves SLOWLY. It is strongly recommended that the EDTA solution be prepared several hours or even the day before you plan on using it. Before use, check the solution to make sure all of the solid has dissolved.2.Using the analytical balance, weigh out ~0.1grams of MgCl2and add the $MgCl_2$ to the EDTA solution. You don't need to wait for the EDTA to dissolve before adding the magnesium chloride.3.Dry about 1 gram of calcium carbonate ($CaCO_3$) in the oven for 2 hours. Transfer to the desiccator and cool (~ 1 hour). When cooled, weigh a 0.5--gram portion of calcium carbonate on the analytical balance and transfer it to a clean 250 mL beaker.4.Add approximately 25 mL of distilled H_2O, then 5mL of conc. HCl carefully o the 250ml beaker. Calcium carbonate reacts vigorously with acid, producing carbon dioxide gas, which may spatter the beaker contents. Cover the beaker with a watch glass. [Note: If

$CaCO_3$ does not dissolve completely, add another 5mL of conc. HCl. When the calcium carbonate has completely dissolved, boil the solution gentlyfor2--5 minutes, keeping the watch glass on the beaker, to expel carbon dioxide. Analytically transfer the solution to a 500.00 mL volumetric flask.]

5. Pipette 25.00 mL of standard Ca^{2+} solution prepared in step 4 into a 250--mL Erlenmeyer flask. Check the pH using pH paper: if acidic, use dilute sodium hydroxide solution to adjust the pH to ~7. When the pH is ~ 7, add 10 mL of 8.5M NH_3-NH_4Cl buffer. This buffer has been prepared for your use. CAUTION!: This buffer is dangerous; it is caustic and ammonia can cause pulmonary paralysis (it can interfere with your ability to breath).

6. Add 20 mL of de-ionized water and 2--3drops of EBT indicator. Titrate the Ca^{2+} standard solution with the EDTA solution until the color changes from wine red, through purple, to a pure rich blue color. At the end point, the last traces of purple in the solution will have just disappeared. If the reaction seems to proceed slowly near the equivalence point, after each addition of EDTA wait a few seconds before adding the next drop.

❖ Estimation of Fe(III) and Al(III) in a mixture by Complexometric titration

- Principle:

Both $Fe^{3+}$and Al^{3+} form 1:1 metal complex with EDTA solution at pH around 5. Now, in between [Al-EDTA]- and $[AlF_6]^{3-}$, the latter is quite more stable while $[Fe\text{-}EDTA]^-$ is more stable than its fluoro-counter part. Thus in a fixed volume of the mixture, whose pH is maintained by addition of acetic acid-acetate buffer (pH~5), if measured excess of standard EDTA is added and the resulting solution is back titrated with a primary standard (zinc acetate or copper sulphate) solution using a suitable indicator (xylenol orange or PAN) then from the titre value, the total amount of Fe3+and Al3+in the given mixture can be determined. Now in the above titrated solution, if ammonium fluoride is added, only the $[Al\text{-}EDTA]^-$ complex is converted to $[AlF_6]^{3-}$, liberating equivalent amount of EDTA that can be estimated by titration with the same titrant as above. Here, the titre value corresponds to the amount of Al^{3+} only in the mixture. The difference of this titre value with the titre value for the total amount of the two metal ions gives the amount of Fe^{3+} in the mixture.

- ✓ Procedure:

  It is suggested that work related to this is to be performed in double distilled water.

  I. Preparation of stock solution:

  The stock solution is prepared in 0.2M H_2SO_4. It should contain about 3.95 g $Al_2(SO_4)_3$. $16H_2O$ and 2.41 g Ferric alum per litre of the stock solution.

  II. Preparation of primary standard Zinc acetate solution:

  250 ml of primary standard M/50 Zinc acetate solution is to be prepared in a volumetric flask in 2% NH4Cl solution (~5 g NH4Cl is to be taken in the volumetric flask and dissolved in some volume, say 50 ml, double distilled water before transferring the weighed amount of Zinc acetate to it).

  III. Standardization EDTA solution:

  25 ml of EDTA solution is pipetted out into a 250 ml conical flask. 25 ml double distilled water is added. 10 ml of acetic acid-acetate buffer (pH~5) is added.

- ✓ Titration using PAN indicator:

  3 drops of PAN indicator are added and the resulting solution is titrated against standard copper sulphate solution. The end point is marked by change of colour from initially yellow to deep green to finally blue. Titration using xylenol orange indicator:

  Alternatively, a pinch of xylenol orange indicator is added (the solution appears yellow) and is titrated against standard zinc acetate solution to a red end point.

- ✓ **Estimation of total amount of Fe(III) and Al(III):**

  25 ml of the stock solution is pipetted out into a 500 ml conical flask. 50 ml of standard EDTA solution is added to it (2 x 25 ml pipetted portions or 50 ml from the burette). Then 1:1

aqueous ammonia is added drop wise, till the solution appears just light orange. The flask is then covered with an inverted glass funnel and placed over a burner or hot plate till it begins to boil. The arrangement is kept in boiling condition for 5 minutes. It is then removed from the source of heating and cooled to 50-60° C. To this 10 ml of acetic acid-sodium acetate buffer is added when the solution should appear yellow. [If it does not become yellow, measured excess of standard EDTA solution is to be added till it appears yellow; one or 2 additional portions of 25 ml pipetted solution of EDTA may be required.]

- Titration using PAN indicator:

3 drops of PAN indicator are added and the resulting solution is rapidly titrated against standard copper sulphate solution. The end point is marked by change of colour from initially yellow to deep green to finally blue.

Titration using xylenol orange indicator: Alternatively, to the resulting solution, a pinch of xylenol orange indicator is added. It is then rapidly titrated against standard zinc acetate solution, (the solution appears yellow) to a red end point.

✓ V. Estimation of Al(III):

To the above titrated solution ~ 1.0 g of solid ammonium fluoride (NH_4F) is added and stirred till the solution turns green. It is then kept in boiling condition as above for a period of 5 minutes and cooled to 50-60° C. 5 ml of acetic acid-acetate buffer (pH~5) is added and the mixture is rapidly titrated against standard zinc acetate or copper sulphate solution using suitable indicator (either PAN or xylenol orange) to detect the end point as above.

❖ **Estimation of Zn(II) in a mixture of Cu(II) and Zn(II)**

Principle:

In a mixture of Cu^{2+} and Zn^{2+} solution, Cu^{2+} can quantitatively be reduced to Cu^{+} by H_2SO_3, while Zn^{2+} remains unreacted:

$$2Cu^{2+} + SO_3^{2-} + H_2O \rightarrow 2Cu^{+} + SO_4^{2-} + 2H^{+}$$

Thus Cu^{2+} can be quantitatively separated from a mixture of Cu^{2+} and Zn^{2+} through reduction of the former followed by its precipitation as CuSCN using H_2SO_3 and NH_4SCN as reductant and precipitant respectively. Zn^{2+}, after separation from Cu^{2+} can be estimated by titrating with standard EDTA solution, either in acetic acid-acetate buffer medium (pH~5) using Xylenol orange indicator or alternatively, in aqueous ammonia-ammonium chloride buffer medium (pH~10) using EBT indicator.

$$2Cu^{+} + 2NH_4SCN \rightarrow 2CuSCN \downarrow + 2NH_4^{+}$$

Procedure:

It is suggested that work related to this is to be performed in double distilled water.

I. **Preparation of stock solution**: The stock solution is prepared in 0.2M H_2SO_4. It should contain about 5.75 g $ZnSO_4.7H_2O$ and 8.32 g $CuSO_4.5H_2O$ per litre of solution.

II. **Preparation of primary standard Zinc acetate solution**: 250 ml of primary standard M/50 Zinc acetate solution is to be prepared in a volumetric flask in 2% NH4Cl solution (~5 g NH4Cl is to be taken in the volumetric flask and dissolved in some volume, say 50 ml, double distilled water before transferring the weighed amount of Zinc acetate to it).

III. **Standardisation of EDTA solution**: 25 ml of Zinc acetate is pipetted out into a 250 ml conical flask. 25 ml distilled water is added.

Titration using EBT indicator:

10 ml of aqueous ammonia-ammonium chloride buffer solution (pH~10) is added followed by a pinch of EBT indicator (the solution appears purple) and is titrated against standard EDTA solution to a sharp blue end point.

Titration using xylenol orange indicator: Alternatively, to the resulting solution, 10 ml of acetic acid-acetate buffer (pH~5) is added followed by a pinch of xylenol orange indicator (the solution appears orange-red) and is titrated against standard EDTA solution to a yellow end point.

IV. Estimation of Zn(II):

25 ml of the aliquot is pipetted out into a 250 ml beaker, provided with a glass rod. The solution is diluted to 95 ml with distilled water and then 1:1 aqueous ammonia is added dropwise, till a permanent bluish white precipitate appears.

5 ml of 4N H2SO4 is added and stirred to have a clear solution. Now about 1.5-2 g Na_2SO_3 is added and the solution is heated so that it just appears to boil, (boiling to be avoided) .This will completely discharge the blue colour of Cu^{2+}. 8 ml of 10% NH4SCN is added to the resulting mixture dropwise with constant stirring to get white precipitate of CuSCN. The solution is left for 20-25 minutes (preferably under warm condition) undisturbed to allow the white precipitate to settle down. It is then filtered through a G-4 sintered glass crucible under gentle suction using a water pump. The original beaker and the residue collected in the crucible are washed with 50 ml hot water. The filtrate along with washing is collected in the same filtering flask and is boiled for 10 minutes to drive out SO_3^{2-} from the mixture as SO_2, completely (to be tested with a filter paper soaked with acidified $K_2Cr_2O_7$, until it does not turn green) from the filtrate. The solution is cooled to room temperature and (1:1) aqueous ammonia is added till a faint smell of ammonia comes out. The resulting solution is then heated to 50-60C.

Titration using EBT indicator:

10 ml of aqueous ammonia-ammonium chloride buffer solution (pH~10) is added followed by a pinch of EBT indicator (the solution appears purple) and is titrated against standard EDTA solution to a sharp blue end point.

Titration using xylenol orange indicator:

Alternatively, to the resulting solution, 10 ml of acetic acid-acetate buffer (pH~5) is added followed by a pinch of xylenol orange indicator (the solution appears orange-red) and is titrated against standard EDTA solution to a yellow end point.

❖ Short General Discussion on Chromatography

Chromatography is essentially a separation process which affects a separation by distributing the sample into two phases. One phase is stationary and second is mobile which flows through the stationary phase. During the process of movement of mobile phase, small differences in adsorption-desorption or partitioning or ion-exchange behaviour of each component of a mixture are multiplied many fold and these parameters distinguish between the different solutes.

There are various ways to classify chromatography.

1. On the basis of physical state of mobile phase the chromatography is classified into two broad groups:

a) Liquid chromatography in which mobile phase used is in the form of a liquid.

b) Gas chromatography in which mobile phase used is a gas.

2. On the basis of physical states of stationary phase and its working principle, chromatography is classified as:

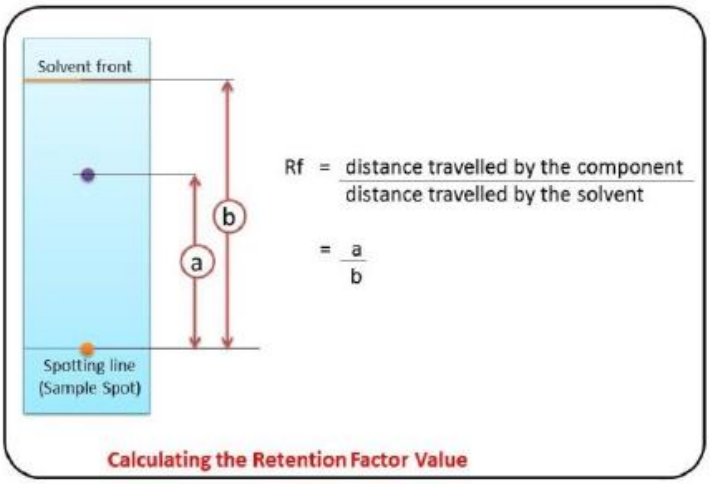
a) Adsorption chromatography in which stationary phase is a solid and works as an adsorbent.

b) Partition chromatography in which stationary phase is a liquid or a liquid supported on an inert solid, and the movement of solute is based on the partition coefficient of the solute into two phases.

c) Ion exchange chromatography in which stationary phase is an ion exchanger and the distribution of solute is based on the ion exchange principle. The concept of R_f Value: R_f value of a solute is the ratio of the rate of movement of the solute peak to the rate of movement of the eluting solvent. However, one cannot readily detect the position of the solvent front or of the solute on the column chromatography. These are better measured now in terms of retention volume or retention time. In paper chromatography Rf value is constantly quoted as a characteristic of the solute. It describes the migration of solute relative to that of eluting solvent and is given by Paper chromatography (PC) is a popular technique for the separation of metal cations. In paper chromatography the principles of partition, adsorption and ion exchange may be exploited, out of these the most important is partition the involves the distribution of a solute between a mobile liquid phase and a gel (a kind of water cellulose complex) as the stationary phase. In paper chromatography, water molecules present in the pores of the filter paper act as the stationary phase and the moving phase can be an eluent like hexane,

toluene, acetone or a mixture of solvents such as methanol-water mixture etc. As the moving phase passes through the spot on which sample has been adsorbed, it dissolves the components more or less readily; depending upon the solubility and carries them along with it while moving on the support. At a given temperature and for a given solvent, it is possible to determine the characteristic rate of movement of each substance on the chromatographic paper, as the moving phase moves. This is represented by relative front or retardation factor also called R_f value. R_f values of different compounds are different even if the mobile phase (solvent) is same. Furthermore, R_f value of a compound may be different in different solvents. Rf values can be calculated by using the above expression. Since solvent front moves faster than the compounds, the Rf value of a substance will always be less than one. Also note that Rf value has no unit. If the compound is coloured then its position on the chromatographic paper may be easily located. However, if the substance is colourless, it may be treated with a developer, which imparts it a characteristic colour.

$$R_f = \frac{\text{distance moved by the centre of the solute zone}}{\text{distance moved by the solvent front}}$$



- **<u>Separation of Ni(II) and Co(II) ions by paper chromatography</u>**

Principle: In between Co(II) and Ni(II), Co(II) readily forms $[CoCl_4]^{2-}$ while Ni (II) does not. Thus the complex $[CoCl_4]^{2-}$ is more soluble in organic solvent dominated mixture like more acetone with less dil. HCl because of covalent nature of the complex species which accounts for the higher R_f value of Co(II) over Ni(II).

Material Required:

1. Whatman filter paper No.1 of large size
2. Glass jar, Rubber cork fixed with hook in the centre
3. Fine capillary tube
4. Spraying bottle
4. Ni(II) and Co(II) solution (1% solution w/v in 1M HCl)
5. Eluting solvent. (Acetone, 6 (M) HCl and water)
6. Developer (mixture of 8-Hydroxyquinoline and Dimethyl glyoxime)
7. Ammonia solution.

- ✓ **Procedure:**

Take a Whatman No. 1 filter paper of size 5 cm x 20 cm. With the help of a pencil, mark a line at a distance of 2 cm from one of the ends of this paper. Put three spot of the Ni(II) solution, Co(II) solution and Ni(II) + Co(II) mixture solution on the marked line with the help of three different fresh and fine

capillary tubes. Hang the filter paper in a jar containing a mixture of acetone, 6.0 M HCl and distilled water, in the volume ratio 86:6:8. Keep the jar as such till the mobile phase (eluent) rises up to two third of the length of the paper. Remove the filter paper from the jar, mark the solvent front. Spray developer solution (2: 1 volume mixture of 8-Hydroxyquinoline and Dimethylglyoxime) on the chromatography paper and damp (do not soak) with 1:1 ammonia to obtain spots of yellow for Co(II) and rose red colour for Ni(II). Mark the position of spots with a pencil and allow the paper to dry. Measure the distance travelled by the solvent front and the different spots of the cations with respect to the reference line. This distance is the shortest distance between the reference line and the centre of different spots. Record the observations in tabular form .Calculate the R_f value for each cation.

❖ Separation of Fe(III) and Al(III) ions by paper chromatography

Principle: Same as for Co(II) and Ni(II). Here Fe(III) easily forming the chloro- complex will have higher R_f value.

Material Required:

1. Whatman filter paper No.1 of large size
2. Glass jar, Rubber cork fixed with hook in the centre
3. Fine capillary tube
4. Spraying bottle
4. Fe(III) and Al(III) solution (1% solution w/v in 1M HCl)
5. Eluting solvent. (Acetone, 6 (M) HCl and water)
6. Developer (8-Hydroxyquinoline)
7. Ammonia solution.

Procedure:

Take a Whatman No. 1 filter paper of size 5 cm x 20 cm. With the help of a pencil, mark a line at a distance of 2 cm from one of the ends of this paper. Put three spot of the Ni(II) solution, Co(II) solution and Ni(II) + Co(II) mixture solution on the marked line with the help of three different fresh and fine capillary tubes. Hang the filter paper in a jar containing a mixture of acetone, 6.0 M HCl and distilled water, in the volume ratio 86:6:8. Keep the jar as such till the mobile phase (eluent) rises up to two third of the length of the paper. Remove the filter paper from the jar, mark the solvent front. Spray developer solution (8-Hydroxyquinoline) on the chromatography paper and damp (do not soak) with 1:1 ammonia to obtain spots of brown for Fe(III) and yellow colour for Al(III). Mark the position of spots with a pencil and allow the paper to dry. Measure the distance travelled by the solvent front and the different spots of the cations with respect to the reference line. This distance is the shortest distance between the reference line and the centre of different spots. Record the observations in tabular form .Calculate the R_f value for each cation.

❖ Gravimetric Estimation of Copper as CuSCN

Principle: Gravimetric analysis is a technique through which the amount of an analyte (the ion being analyzed) can be determined through the measurement of mass. **Gravimetric** analyses depend on comparing the masses of two compounds containing the analyte.

Precipitative gravimetric analysis requires that the substance to be weighed be readily removed by filtration. In order for a non-filterable precipitate to form, it must be supersaturated with respect to its solubility product constant. However, if it is too far above the saturation limit, crystal nucleation may occur at a rate faster than crystal growth (the addition of molecules to a crystal nucleus, eventually forming a non-filterable crystal). When this occurs, numerous tiny micro-crystals are formed rather than a few large ones. In the extreme case, micro-crystals may behave as colloids and pass through a fibrous filter. To avoid this, precipitating solutions may be heated. Because the solubility of most salts increases with increasing temperature, this treatment will lower the relative degree of super saturation and slow the rate of nucleation. Also, one might add the precipitant slowly with rapid mixing to avoid the occurrence of locally high concentrations.

Precipitative gravimetry is often practiced at high ionic strengths. This is to reduce the electric double layer thickness (salting-out effect) of the slowly forming crystals. When this occurs, electrostatic repulsion between the crystal and its precipitating molecules is reduced. Crystal growth can then occur more rapidly. It is very important that the precipitate be pure and has the correct stoichiometry.

Copper can be gravimetrically estimated as cuprous thiocyanate. When a known volume of Cu^{2+} solution is reduced to Cu^{+} by sulphurous acid and treated with an excess of ammonium thiocyanate solution, CuSCN gets quantitatively precipitated.

$$2Cu^{2+} + SO_3^{2-} + H_2O \rightarrow 2Cu^{+} + SO_4^{2-} + 2H^{+}$$

$$2Cu^{+} + 2NH_4SCN \rightarrow 2CuSCN \downarrow + 2NH_4^{+}$$

- ✓ Preparation of the stock solution:

The stock solution should contain about 8.0 g $CuSO_4$. $5H_2O$ per litre of solution.

II. **Procedure:**

25 ml of the aliquot is pipetted out into a 250 ml beaker, provided with a glass rod. The solution is diluted to 95 ml with distilled water and then 1:1 aqueous ammonia is added dropwise, till a permanent bluish white precipitate appears. 5 ml of 4N H2SO4 is added and stirred to have a clear solution. Now about 1.5-2 g Na2SO3 is added and the solution is heated so that it just appears to boil, (boiling to be avoided) .This will completely discharge the blue colour of Cu^{2+}. 8 ml of 10% NH_4SCN is added to the resulting mixture drop wise with constant stirring to get white precipitate of CuSCN. The solution is allowed to stand undisturbed for 20-25 minutes (preferably under warm condition) for settling of the white precipitate (the completeness of the precipitation should be checked by adding a few drops of NH4SCN to the supernatant liquid). It is then filtered through a previously dried and weighed sintered glass (G-4) crucible using a policeman for quantitative transfer of the precipitate under gentle suction that uses a water pump. The residue collected in the crucible is washed with 50 ml hot water containing 0.01% NH_4SCN and 1% Na_2SO_3 and a few drops of dil H_2SO_4. The crucible is dried with its content at 110-120°

C. Drying and weighing cycles are repeated until constant weight is obtained. The concentration (g/dm3) of copper in the solution is to be calculated from the difference in weight of the empty crucible and the crucible with the precipitate.

❖ Gravimetric Estimation of Aluminium as $Al(oxine)_3$

Principle: Aluminium is estimated gravimetrically as tris (8-hydroxiquinolinato)aluminium(III). 8-hydroxyquinoline is generally known as oxine. Thus if a known volume of Al3+ solution is treated with a slight excess of oxine solution at pH~ 5 , $Al(Oxine)_3$ gets quantitatively precipitated .

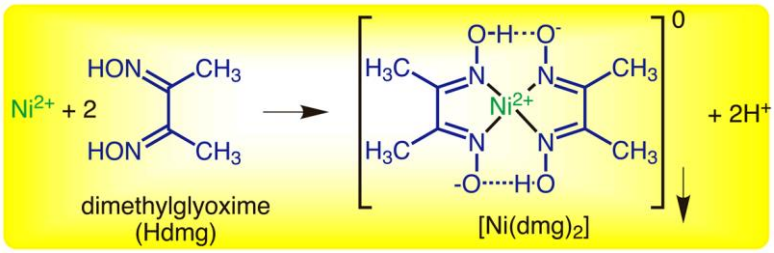
Preparation of Aluminium Solution: 16 gm aluminium ammonium sulphate is dissolved in 1000 cm^3 of water.

Procedure: 25 cm3 of the aluminium solution is pipetted out into a 250 cm3 beaker. 75 cm3 of distilled water is added followed by 5 cm3 10% tartaric acid solution. The mixture is neutralized with 1:1 aqueous ammonia solution and then 10 cm3 of Acetic acid – Sodium Acetate buffer solution is added to it. The resulting mixture is heated nearly to boiling and 2% solution of oxine (8-hydroxyquinoline) in 2 M acetic acid is slowly added until the precipitation is complete. The mixture is allowed to stand for 25 to 30 mins in warm condition within which the precipitate settles down. (The supernatant liquid should be faintly yellow at this stage, indicating that oxine is present in slight excess). The precipitate is filtered under mild water suction through a previously dried and weighed sintered glass (G-4) crucible using a policeman for quantitative transfer of the precipitate. It is washed thoroughly with hot distilled water until the washing is free from oxine (Test with freshly prepared aqueous solution of FeCl3 shows green colour with oxine), dried at 110 - 120°C, cooled and weighed. Drying and weighing cycles are repeated until constant weight is obtained. The concentration (g/dm3) of aluminium in the solution is to be calculated from the difference in weight of the empty crucible and the crucible with the precipitate.

Gravimetric determination of nickel in an unknown solution *using DMG*

Procedure:

Clean a sintered glass crucible (G-4) and then dry it at 110-120° C in air oven for about 10 minutes, then cool in a desiccator for 10 minutes and weight the empty crucible. Repeat the process of heating, cooling and weighing until a constant weight is attained (±0.0010 g).



Take an aliquot of 10 ml of supplied Ni(II) solution into a 250 ml beaker. Dilute to 150 ml with distilled water. Heat to 70-80° C on a hot water bath, add 20 ml of 1% dimethyl glyoxime solution and mix throughout by stirring with a clean glass rod. Neutralize with (1:1) aqueous ammonia solution by adding dropwise with constant stirring until the smell of ammonia persists and a red-rose precipitate of $Ni(DMGH)_2$ is formed. Cover the beaker with a watch glass and allow to stand on a hot water bath (do not boil but feel hot from outside of the beaker) for about 20 minutes. Check the completeness of precipitation by adding a few more drops of the dimethyl glyoxime reagent solution to the supernatant liquid, smelling faintly of ammonia.

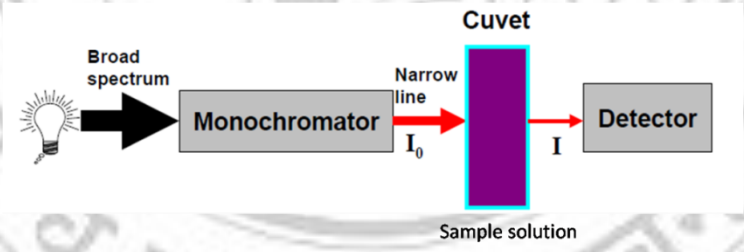
Filter the precipitate using the previously dried and weighed sintered glass (G-4) crucible. Wash the precipitate with hot distilled water until it is free from unwanted chloride or sulphate [test with $AgNO_3$ and $Ba(NO_3)_2$ solution in nitric acid medium]. Dry the crucible with its contests at 110-120°C for about 45 minutes in air oven. Allow to cool in a desiccator for 15 minutes and then weigh. Repeat the procedure of heating, cooling and weighing until constant weight is attained. Calculate the strength of supplied Ni(II) solution in **gm/lit**.

- **Estimate Fe(III) in µg in the supplied Sample Solution Calorimetrically as $[Fe^{III}(SCN)]^{+2}$ Complex.**

Theory:

The Beer-Lambert Law:

The absorption of photons of light is described by the Beer-Lambert Law, *a relationship indicating a linear relationship between concentration and absorbance.*



The Beer-Lambert law states that the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution.

The law states that:

$$A = \varepsilon l c$$

Where:

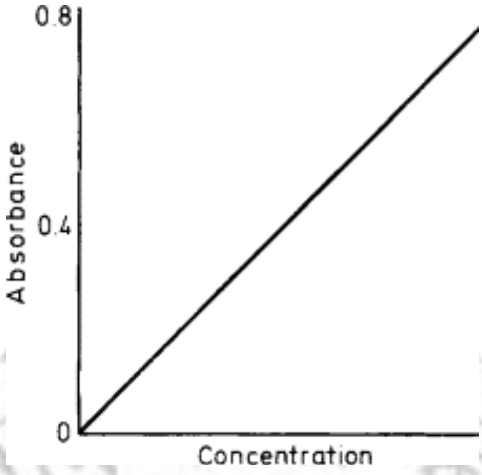
ε= *molar absorption coefficient or* molar extinction coefficient [if the concentration is measured in moles/liter; unit: $dm^3\ mol^{-1}\ cm^{-1}$ in CGS unit].

C=concentration of the absorbing material (mol dm^{-3}),

l= thickness of the absorbing layer (cm)

A= absorbance (unit less)

The absorbance is inversely proportional to the transmittance of the solution. Generally, **dilute** solutions follow the Beer--Lambert Law Quite well.



Procedure:

i) Prepare 100 ml M/50 $Zn(OAc)_2$ in 2% NH_4Cl.

ii) Standardized the supplied M/50 EDTA with NH_4Cl- NH_4OH buffer and EBT indicator as usual.

iii) Standardized the supplied Fe(III) solution by M/50 EDTA by the procedure given bellow:

Take 10 ml of the M/50 Fe (III) solution in 100 ml conical flux and add dilute NH_3 solution drop wise with shaking until a faint turbidity appears. Dissolve the ppt with 1-2 drops of dilute HCl and add 3-4 drops of KSCN/NH_4SCN indicator. Titrate with standard M/50 EDTA till the colour changes from red to colourless.

iv) Dilute the standardized Fe(III) solution to exactly 10^{-3}M (100 ml).

v) Take **0.5, 1, 1.5, 2, 2.5 ml** portions of the 10^{-3} M Fe(III) solution in 25 ml volumetric flux. Add 5 ml KSCN/NH_4SCN solution and make up the volume with 0.02 M HNO_3.

vi) Take any one of this solution and determine absorbance at different wave length (**700-400** nm) and hence **find** λ_{max} or **the best filter** (at the case may be) as usual.

vii) Measure the absorbance of the prepared solutions at λ_{max} or the best filter.

viii) **Calibration Curve:** Plot the **O.D** Vc. **Conc.** of Fe(III) and draw the best straight line through the origin and the experimental points.

ix) Treat the unknown Fe(III) supplied with 10 ml KSCN/NH_4SCN indicator and make up the volume with 0.01 M HNO_3 and measure the O.D at λ_{max} or the best filter and hence find the concentrations from the Calibration Curve. Calculate Fe(III) supplied in **μg**.

❖ **Inorganic Preparation of Salts and complex**

- : **PREPARATION OF POTASH ALUM**

Procedure:

Weigh 10.0 g aluminium sulphate and powder it. Transfer to a 150 cm3 beaker. Dissolve in 25 ml distilled water containing 2ml concentrated sulphuric acid. Warm to dissolve and add more H_2SO_4 acid if necessary to get a clear solution. Weigh 3.0 **g** potassium sulphate and powder it. Transfer to another 150 ml beaker. Add 25 ml distilled water. Stir to dissolve. Warm if necessary. Filter the two solutions through a previously moistened paper into an evaporating dish.

Heat the solution on a wire gauze and concentrate the solution to the crystallisation point, till the rod dipped in the solution deposits a crust on it. Cover with a watch glass and allow the solution to crystallise. When the crystallisation is complete, decant the mother liquor and wash the crystals with 5 **ml** ice cold distilled water. Dry the crystals by pressing them gently between pads of filter papers. Allow to dry on a porous plate. Weigh the crystals and record the yield. Calculate the percentage yield.

- **PREPARATION OF TETRAAMMINECOPPER(I1) SULPHATE MONOHYDRATE:**

Weight out 2.0 g copper(I1) sulphate and powder it. Add powdered crystals to a 250 ml beaker. Prepare ammonia solution by adding 10 ml ammonia to 5 ml distilled water. Slowly add ammonia solution to the powder with stirring until all the copper(II) sulphate dissolves resulting in a deep blue solution. Add 1-2 cm3 of ammonia solution in excess. Add ethanol dropwise and with stirring till a deep blue precipitate is formed. Heat the beaker on a water bath at 60°C. stir and wait till the blue precipitate just dissolves. Cover the beaker with a watch glass and set aside to crystallise. Beautiful dark blue needle like crystals separate after 1 hour. Filter off the crystals using a Buchner funnel and wash with 2-3 ml ethanol at the pump. Allow the air to pass for 5 minutes. Transfer the product to a watch glass and dry in a desiccator. Store the crystals in a weighed weighing bottle.
Weigh the dry crystals. Calculate the percent yield.

- **Preparation of $K_3[Fe(ox)_3].3H_2O$ [TRIOXALATO-FERRATE(III) TRIHYDRATE]**
  Procedure

A. Preparation of $FeC_2O_4.2H_2O$: Dissolve 7.5 gm of Mohr's salt in 25 ml of 2% H_2SO_4 solution. In a 250 ml beaker dissolve 5 gm of oxalic acid in 2% H_2SO_4 and the Mohr salt solution into it with stirring. Pleace the reaction mixture on an asbestos board and heat without stirring and bring to mild boiling. Allow to cool to room temperature, when yellow crystals of $FeC_2O_4.2H_2O$ salt out. Decant off the clear supernatant liquid.

B. **Preparation of Final Complex**: Dissolve 5 gm of $K_2C_2O_4.H_2O$ in 15 ml water and suspend the crystals of $FeC_2O_4.2H_2O$ into this solution. Place the mixture on a hot water bath and bring to about 40° C. To this hot solution add 12.5 ml H_20_2 (30%) drop wise from a burette with constant stirring during addition. Place the reaction mixture on an asbestos board and heat to boiling, some brown ppt may form at this stage. Add at a time 10 ml of 10% oxalic acid solution to the boiling reaction mixtures to dissolve this ppt (add few more drops if necessary).The reaction mixture should be boiling during this addition. Filter the hot reaction mixture and add 10 ml MeOH to the filtrate. If any solid separate in this stage, dissolve it by gentle warming. Allow the Reaction mixture to stand in the dark and collect the green crystals under suction and wash with 1:1 MeOH/H_2O.Dry in air and record the yield and submit the product in a stoppered test tube.

Report the yield of the product and submit the crude product.

- **Synthesis of hexaammine cobalt(III) chloride:**

Requirements: 1. Cobalt (II) chloride hexahydrate 2. Hydrogen peroxide 3. Ammonium chloride 4. Ammonia 5. Hydrochloric acid 7. Sulphuric acid 6. Activated charcoal.

Procedure:

Dissolve ammonium chloride (1.2 g, 2.2 mmol) in water (3 ml). Heat the paste till it starts boiling. Add cobalt(II) chloride hexahydrate (1.8 g, 7.5 mmol) to the paste. Take activated charcoal (0.2 g) in a separate flask and add the paste to this. Cool the flask and its contents under running water. Add concentrated ammonia (4.5 ml, 20% v/v) to the solution and cool the mixture to 10^0 C (approximately). Add slowly hydrogen peroxide (2.4 ml, 30% v/v) to the solution with a dropper. Swirl the flask gently during the addition. Heat the solution on steam bath at 50-60^0 C until the pinkish tint disappears from the solution (~20 min). Cool the solution in an ice bath and filter through a Büchner funnel. Transfer the residue to a boiling solution of hydrochloric acid (15 ml, 0.5 M). Heat the solution with stirring until the solution boils and filter the hot solution using a Büchner funnel under suction. Filter the precipitate and dry the product at 110^0C for an hour. Calculate yield.

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PART – III: LABORATORY MANUAL FOR ORGANIC CHEMISTRY

CONTENTS

ORGANIC QUALITATIVE ANALYSIS

PHYSICAL CHARACTERISTIC OF SAMPLE:

Note the obvious physical properties: Colour, State, Odour and Solubility.

COLOUR:

- **Yellow**: Quinones, 3 and 4-nitroaniline, 2-nitrophenol and many other nitro compounds, iodoform (Note that some nitro compounds often appear yellow but colourless when absolutely pure)
- **Orange**: 2-Nitroaniline, Phenanthaquinone and Alizarin.
- **Red**: 1, 2-naphthaquinone

ODOUR:

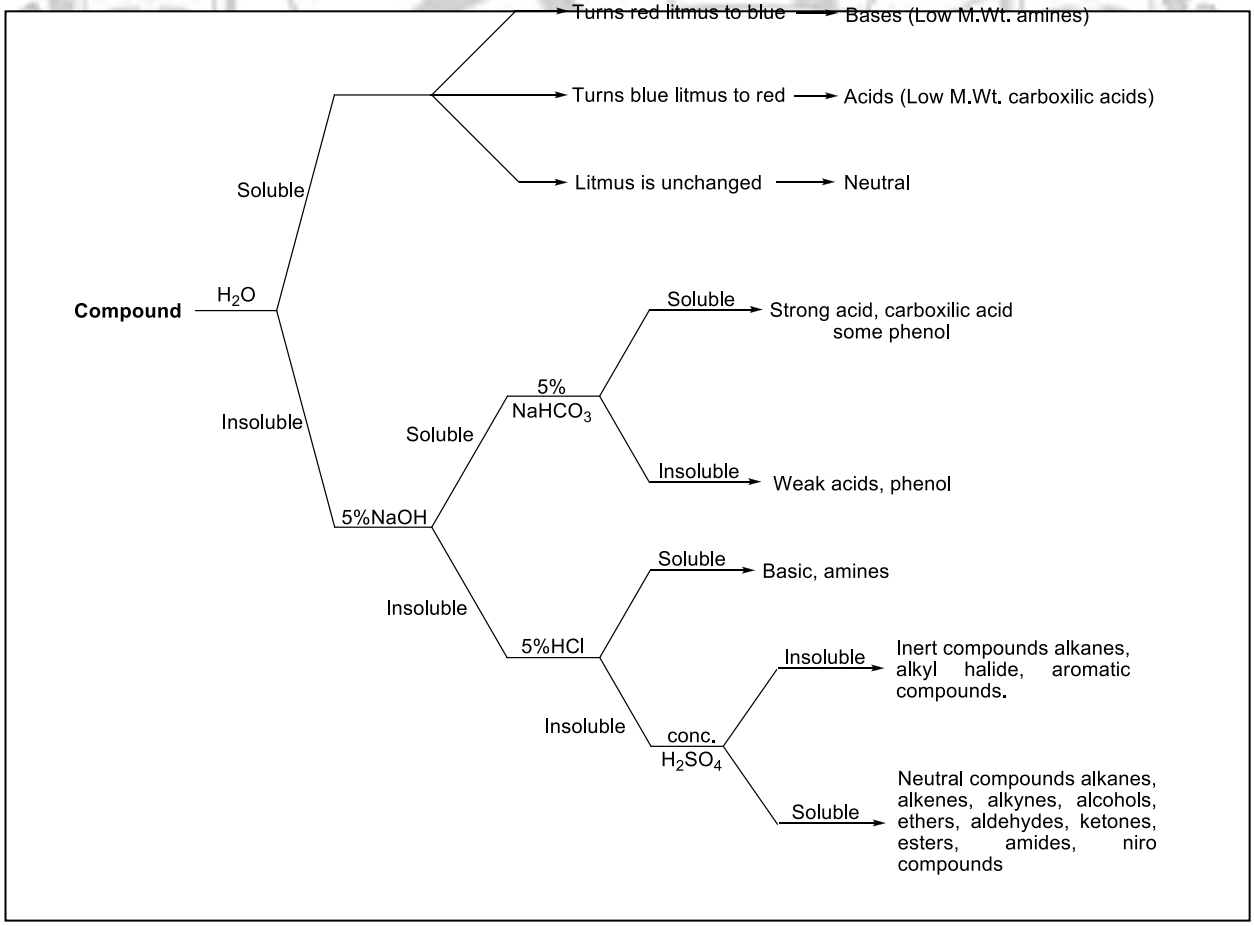
- **Pleasant** (often fruity) **odour**: Ester and ethers
- **Pungent odour**: Formic acid, Acetic acid, Acetyl chloride, Acetic anhydride, Benzoyl chloride, Benzyl chloride, Pyridine, Benzoquinone (when warmed with water).
- **Phenolic odour**: Many phenols, some derivative of salicylic acid.
- **Odour of almonds**: Benzaldehyde, Benzonitrile, Nitrobenzene.

Some substances posseses odour which are not characteristic.

SOLUBILITY TEST:

- Solubility test should be performed on every unknown compound.
- They are extremely determining the nature of major functional groups present in unknown compounds.
- The solubility test will reveal whether the compound is strong base (amine), weak acid (phenol), a strong acid(carboxylic acid), or neutral substance (aldehyde, ketone, alcohol and ester)
- The common solvent used are water, 5% HCl, 5% $NaHCO_3$, 5%NaOH, conc. H_2SO_4 and ethanol.

SOLUBILITY TEST:



PROCEDURE:

Place about 1 ml of solvent in a small test tube

↓

Add one drop of an unknown liquid sample from a dropper or a few crystal of unknown solid directly into the solvent.

↓

Gently tap the test tube with your finger to assure mixing.

↓

Observed whether any mixing line appear in the solution (the disappear of the liquid or solid of the mixing lines, indicates the solution is taking place)

↓

Add several or more drops of the liquid, or a few more crystals of the solid, to determine the extent of compound solubility.

COMMON ERROR ALERT!

A common mistake made in determining the solubility of a compound is testing with a quantity of the unknown too large to dissolve in the chosen solvent.

- Use small amounts
- Compounds in the form of large crystals will require more time to dissolve the powder than powder or very small crystals.
- It is helpful to pulverize a compound with large crystals in a mortar and pestle.
- Gently heating is helpful in some instances, but strong heating is to be **discouraged**, as it often leads to reaction.
- When the coloured compound is dissolve, the solution will often assume the colour.

Using the procedure given above, the solubility the solubility of the unknown should be determined in each of the following solvents such as, Water, 5% HCl, 5% $NaHCO_3$, 5%NaOH, conc. H_2SO_4 and ethanol, a colour change may be observed rather than solution.

A colour change should be regarded as a positive solubility test.

- Compounds soluble in water will usually be soluble in all of the aqueous solvents.

Solubility in 5% HCl:

If a compound is soluble in dilute acid (5% HCl), we expect the possibility of amine should be considered immediately.

- The hydrochloride or sulphate salt of amines are soluble in water.
- Some very high molecular weight amines, like tribromo-aniline may also be insoluble in dilute acid.

Solubility in 5% $NaHCO_3$ and 5% NaOH:

One can distinguish between weak and strong acids by determining their solubility in both strong (NaOH) and weak ($NaHCO_3$) base. The classification of some functional groups as either weak or strong acid is given in the accompanying table.

Strong acids	Weak acids
Soluble in both NaOH and $NaHCO_3$	Soluble in NaOH but not $NaHCO_3$
• Sulphonic acids: RSO_3H	• Phenols: ArOH
• Carboxylic acids: RCOOH	• Imides: RCONHCOR
• *Ortho* and *para* substituted *di-* and *tri-* nitrophenol.	

For the purposes of this experiment, carboxylic acids (pKa ≈ 5) are generally indicated when a compound is soluble in both bases, while phenols (pKa ≈ 10) are indicated when it soluble in NaOH only.

- In phenols, substitution of nitro groups in the *ortho* and *para* positions with respect to –OH group, increases the acidity.
- Phenols which have two or three nitro group in the ortho and para positions will often dissolve in both NaOH and $NaHCO_3$ solutions.

Solubility in conc. H_2SO_4:

Many compound are soluble in cold conc. H_2SO_4 of the compounds included in the experiment, ketones, aldehydes, alcohols and esters are in this category. Other compounds which also dissolve include alkenes, alkynes, ethers nitroaromatic and amides.

DETECTION OF SPECIAL ELEMENTS

(N, S and Cl, Br, I)

In order to detect these elements in organic compounds, it is necessary to convert them into ionisable inorganic substances so that the ionic test of inorganic qualitative analysis may be applied. This conversion may be accomplished by several methods, but the best procedure is to fuse the organic compound metallic sodium (Lassaigne's test).

Lassaigne's test:

A small piece of clean metallic sodium was heated to melt in a clean dry fusion tube. Now a small quantity of given organic sample was added in portions over molten sodium and tube was again strongly heated till red hot. It was plunged to 10 ml of distilled water taken in a porcelain mortar and ground thoroughly with a pestle (A vigorous actions occurs as the tube fractures and excess sodium oxide reacts with water: hence need to hold), filtered and following test were performed with this filtrate.

Test for 'N':

Experiment	Observation	Inference
2-3 ml of filtered fusion solution is taken into a test tube containing 0.1-0.2 gm of powdered $FeSO_4$ crystals. The mixture was gently heated with shaking until boils, then without cooling sufficient dil. H_2SO_4 is added to dissolve the iron hydroxide and give the solution an acid reaction.	A Prussian blue precipitation or colouration.	'N' is present

If sulphur is present, a black Precipitation of FeS is obtained when the $FeSO_4$ crystal is dissolve, it is not necessary to filter off the black precipitation. The fusion filtrate is heated for about 30 seconds by further adding small amount of $FeSO_4$ crystals then sufficient amount of H_2SO_4 is added to dissolve the precipitation.

Test for 'S':

Experiment	Observation	Inference
A small amount of fusion solution is acidified with dil. H_2SO_4 and few drops of lead acetate solution is added to it.	Black ppt.	'S' present.
To a small amount of fusion solution and 2-3 drops of freshly prepared sodium nitoprusside solution is added	An intense purple colouration which slowly fades on standing.	'S' present.

Test for 'HALOGENS':

Experiment	Observation	Inference
2-3 ml of filtrate is acidified with dil. HNO_3, and is evaporated to half of the original volume in order to expel the HCN/ or H_2S which may be present. Then it is diluted with the equal		

volume of water. Now to this solution excess $AgNO_3$ is added. The mother liquor is decanted off and the precipitate is treated with dil. NH_4OH solution.	White precipitate of AgCl, and readily soluble in the NH_4OH solution. Off white precipitate of AgBr, and difficulty soluble in NH_4OH solution. Yellow precipitate of AgI, and insoluble in NH_4OH solution.	'Cl' is present. 'Br' is present. 'I' is present.

If off white or yellow ppt^n is obtained in the $AgNO_3$ test perform Layer Test to confirm 'Br' or 'I' or both.

Layer Test:

A small amount of the fusion solution is acidified with dil. H_2SO_4 and boil it about 2 minute, and about 1 ml of CCl_4 is added to the solution after cooling.

EXPERIMENT	OBSERVATION	INFERENCE
If halogen is present carry out the following test: 1ml of extract + 1ml of dilute H_2SO_4 +0.5ml of $CHCl_3$ and 0.5ml of chlorine water ,shake well and observe the colour of chloroform layer	Violet colour	Iodine present.
	Yellow or brown colour.	Bromine present.
	Colourless layer.	Chlorine present.

Detection of Functional Groups

Test for Carboxylic acids (-COOH):

EXPERIMENT	OBSERVATION	INFERENCE
(a) 0.1gm of substance +3 ml Saturated $NaHCO_3$ solution. Shake well. The substance dissolves. To this clear solution add conc. HCl drop by drop.	Strong effervescenc A solid appear	Carboxylic acid present. Carboxylic acid confirmed.
(b) 0.05 gm of compound + 1ml of water , shake well + 1-2 drops of alcoholic $FeCl_3$ solution.	1. Buff coloured precipitate	Benzoic acid or phthalic acid.
	ii. Violet coloured precipitate	Salicylic acid
	iii. Violet coloured precipitate obtain on heating the solution	Acetyl salicylic acid
	iv. Yellow coloured precipitate	Cinnamic acid
	v. Faint reddish coloured precipitate	Succinic acid
	vi. Deep yellow coloured solution	Citric acid
	vii. No change in FeCl3 solution.	Oxalic acid

Test for Phenolic -OH:

EXPERIMENT	OBSERVATION	INFERENCE
(a) 0.1gm of substance +3 ml dilute NaOH solution. Shake well. To this clear solution add conc. HCl drop by drop.	Compound dissolves completely. A solid or emulsion appear	Phenol present
(b) **Back Dye Test:** A few drop of aniline is dissolve in dil. HCl cool in ice water, few drops of cool dil. $NaNO_2$ solution. The clear solution is added to cold solution of O.S. in NaOH.	Brilliant red Dye	Phenolic –OH group is present
(c).0.01gm of compound + 3ml of water or alcohol shake well and add a drop of alcoholic or neutral FeCl3 solution.	i. Violet Colour	Phenol Present
	ii. Blue Violet Colour	Resorcinol
	iii.White ppt slowly changing to pink, blue or violet	α - napthol
	iv. Green Colour	ß - napthol
(d).**Phthalein Test:** 0.01gm of compound + 0.01gm of phthalic anhydride + 2 drops of conc. H_2SO_4.Heat gently until the mixture fuses. Cool and pour it in a beaker containing 20 ml of very dilute NaOH solution.	Pink colour	Phenol Present
	Green or bluish green	α – napthol β – napthol
	Yellowish-green flouresence	Resorcinol
(ed). **Liebermann Test:** 0.01gm of compound+1ml of conc. H2SO4 + 2 crystal of NaNO2. Heat it gently. Dilute it with water , add 20% NaOH solution.	Red colouration Bluish greenish coloration	[F.G -OH (Phenolic)]

Test for Aaldehydes and Keto Carbonyl (-CO-) groups:

EXPERIMENT	OBSERVATION	INFERENCE
0.05 gm of the compound + 3 ml of 2, 4 dinitrophenyl hydrazine. Shake well.	Yellow or orange red crystalline precipitate	Aldehyde or Ketone Present
If this test is positive, perform the following test to distinguish between aldehyde and ketone.		
EXPERIMENT	**OBSERVATION**	**INFERENCE**
Test for Aldehydes : (a) **Schiff's Test:** 0.05 gm of the compound + 2/3 ml of Schiff's Reagent .Shake well.	Viotet colour immediately develops	Aliphatic aldehyde present
	Pink colour slowly develops	Aromatic aldehyde present
(b) **Tollen's Test OR Silver Mirror test:** 0.1 gm of the compd +2-3mlTollents reagent (i.e. Ammonical silver Nitrate solution) + Heat it on a boiling water bath.	A silver mirror is formed on the inner sides of the test tube.	Aldehyde present
(c) **Fehling Solution Test:** 0.1gm of the compd + 1ml Fehling A + 1ml Fehling B solution .Heat it gently.	Formation of red ppt of Cuprous Oxide(Cu_2O).	Aldehyde present

(d) **Benedict's test:** 0.1gm of the compd + Benedicts solution + Heat it gently.	Formation of red ppt Cuprous oxide	Aldehyde present

Fehling's and Tollen's reagents are reduced by α-hydroxyketones. i.e. having
The carbonyl compound is ketone if above tests for an aldehydes is negative

EXPERIMENT	OBSERVATION	INFERENCE
Teat for Ketones : (a) 0.1gm of compd + 2ml of sodium nitroprusside solution + 2 drops of NaOH	Wine Red colour or Orange red colour CH3-CO- gr gives this test.	Ketone present

Preparation of acetanilide:

Method 1: Distilled aniline (9.3 g; 0.1 mol; 10 ml) and glacial acetic acid (10 ml) into a round bottomed flask (100 ml) equipped with a reflux condenser. Add zinc dust (ca. 0.1 g), boiling chips and acetic anhydride (10.2 g; 0.1 mol; 10 ml) to the aniline solution, and heat the mixture gently for 30 min. Pour the resulting mixture in its warm state into cold water (250 ml), and cool the forming suspension in ice water properly. Filter off the forming solid on Büchner funnel or sintered glass funnel, and wash it with cold water (2 × 20 ml). Dry the dewatered solid at room temperature in air (yield of the air-dried crude product is 10-11 g).

Recrystallize the air-dried crude product from water (20 ml water/g product, boiling chips, an Erlenmeyer flask on a heating plate-tripode heated by a Bunsen burner, in case of significant coloring, apply decolorizing carbon). Collect the filtrate from the hot filtration (performed over a folded filter paper) in an Erlenmeyer flask and allow to cool. Filter off the forming crystalline product, wash it with cold water and let it dry in air. The yield and melting point of the product should be determined from the dry recrystallized material.

Method 2: Dissolve aniline (5.0 g; 0.054 mol, 5 ml) in a mixture of water (135 ml) and concentrated hydrochloric acid (4.5 ml; 0.054 mol). In case of significant coloring (if the solution do not remain not colorless or only pale yellow), decolorize the solution by charcoal. Prepare a solution from anhydrous sodium acetate (5.3 g; 0.065 mol) and water (30 ml). Add acetic anhydride (6.2 ml; 0.065 mol) to the stirred acidic aqueous aniline solution. After addition of the acetic anhydride, add the sodium acetate solution in one portion to the reaction mixture. Cool the resulting mixture in ice-water with occasional stirring for about 30 min. Filter off the forming solid on Büchner funnel or sintered glass funnel, and wash it with cold water (2 × 15 ml). Dry the dewatered solid at room temperature in air (yield of the air-dried crude product is about 6.5 g).

Preparation of m-Dinitrobenzene:

An acid mixture is prepared by mixing conc. HNO3 (20 ml) and conc. H2SO4 (20 ml) in portions in a 500 ml RBF with shaking and then the mixture is cooled. Nitrobenzene is added in small portions (2 ml at a time) shaking the flask after each addition to ensure through mixing. The flask is than fitted with an air condenser and heated on boiling water bath with frequent shaking until a drop of the liquid solidifies when add into a small quantity of cold water (the duration of heating is about half an hour). Separation of a hard, pale yecake of m-dinitrobenzene indicate the completion of reaction; on the otherhand separation of semi-solidss requires further heating. The contents of the flask, while m is poured into 300 ml of ice-water stirring. The solid is filtered under suction, washed thoroughly with cold water, recrystallised from rectified or methylated spirit and dried. The yield of the air-dried crude product is 11 g.

Single Compound Detection : Liquid Samples

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless

Odour : Pungent but faintly alcoholic

Litmus : The sample is neutral to litmus

Action of heat : completely volatilise without having any residue.

Ignition Test : Produce blue non sooty flame, i.e. the sample is not aromatic compound.

Miscibility with water : The sample is freely miscible with water.

Preliminary Conclusion : Since the sample is colourless liquid, miscible with water and neutral to litmus, it may be either ethanol or methanol or acetone. The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or liquid but immiscible with water (like benzaldehyde, chloroform, nitrobenzene, aniline or dimethylaniline). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. A Cu-spiral is made repeatedly red hot and introduced in 1-2 ml of the sample taken in a test tube. It is divided in two parts. (a) Part 1 + Schiff's reagent, shaken vigorously. (b) Part II + Tollen's reagent,warmed on water bath.	Pink colour is developed which deepers gradually. Bright silver mirror formed on the inner wall of the test tube.	May be ethanol or methanol. May be methanol or ethanol.
2. **Legal's Test :** A few drops of very dilute solution of sodium nitroprusside is added to 2-3 ml of aq. Solution of the sample followed by a few drops of dil. NaOH solution.	No ppurple/ ruby red colour is developed.	Acetone absent.

3. Iodoform Test : To 1-2 ml of the sample a strong solution of iodine in aq. KI solution is added. Now to it a dilute solution of NaOH is added dropwise until the violet colour is disappeared. The mixture is then warmed in water bath and then cooled under tap.	No characteristic yellow ppt. of iodoform resulted.	May not be acetone or ethanol.The sample may be methanol.
4. Denig's Test : To about 5 ml of aq. Solution of the sample taken in porcelain basin or conical flask, 3-4 ml of dilute $KMnO_4$ solution is added with cooling in ice water. To it few drops of conc. H_2SO_4 is added when a brown colour is developed. This brown color is destroyed by addition of saturated solution of oxalic acid. Now, to it freshly prepared Schiff's reagent is added and allowed to stand with occasional stirring.	A violet colour is developed within 3-5 minutes.	Methanol present and confirmed.
5. Oil of Wintergreen Test: 2-3 ml of sample is added to 0.5 gm of salicylic acid and it is heated for 2-3 minutes after addition of 5-6 drops of conc. H_2SO_4. After cooling, The mixture is poured into about 50 ml of water taken in a beaker and then neutralised with sodium bicarbonate.	An oily layer with a characteristic smell of methyl salicylate is formed over the water.	The sample is methanol- it is confirmed.

Conclusion : The supplied sample is methanol.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless

Odour : Characteristic smell of bitter almonds.

Litmus : The sample is neutral to litmus. (An old sample changes blue litmus to red).

Action of heat : completely volatilise without having any residue.

Ignition Test : Produce yellow sooty flame, i.e. the sample is aromatic compound.

Miscibility with water : The sample is immiscible with water and also immiscible with dil. HCl.

Preliminary Conclusion : Since the sample is colourless liquid, neutral to litmus, immiscible with water and dil. HCl, so it may be one of the following liquid samples:

(i) Benzaldehyde
(ii) Nitrobenzene
(iii) Chloroform

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or liquid but miscible with dil.HCl (like aniline or dimethylaniline). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. Little of the sample + Conc. KOH solution, boiled and acidified with conc, HNO_3, filter if necessary, to the filtrate, $AgNO_3$ solution is added.	No curdy white ppt. formed.	Chloroform absent.
2. **Carbylamine Test :** Sample + few drops of aniline +2 ml of ethanolic KOH solution, heated.	No obnoxious smell of carbylamines(phenyl isocyanide) is evolved.	Chloroform absent.
3. **Reduction and the dye test :** Little of the sample + conc. HCl (3-5 ml) +Zn-dust (pinch by pinch), warmed and filtered. Filtrate cooled + cold dil.	No characteristic red or orange dye formed.	Nitrobenzene absent.

$NaNO_2$ solution dropwise. Now this solution is added to cold alkaline solution of β-naphthol.		
4. **Brady's Test :** To an alcoholic solution of the sample, Brady's reagent (2-3 ml) and a drop of conc. H_2SO4 is added. Warmed and cooled if necessary.	Reddish yellow crystalline ppt. formed almost immediately.	Benzaldehyde may be present.
5. **Schiff's Test :** Litle of the sample or its alcoholic solutionis added to cold, freshly prepared Schiff's reagent and shaken well.	A pink colour is developed.	May be benzaldehyde.
6. **Tollen's Test :** Alcoholic solution of the sample is added to Tollen's reagent and warmed on water bath.	A shining silver mirror is formed at the wall of the test tube.	Benzaldehyde present.
7. **Cannizzaro Reaction :** Little of the sample is boiled with conc. NaOH for 3-5 mins., aq. Part separated and acidified with dil. HCl.	White ppt. formed.	Benzaldehyde present.
8. **Malachite Green test :** Little of the sample is heated in a dry test tube with few drops of *N,N*-dimethylaniline and a bead of anhydrous $ZnCl_2$(solid). After cooling acetic acid and PbO_2 is added to it, shaken well and then conc. HCl is added to it.	An intense green colour is developed.	Benzaldehyde present and confirmed.

Conclusion : The given sample is Benzaldehyde and its structure is Ph-CHO.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless

Odour : Sweet smelling

Litmus : The sample is neutral to litmus

Action of heat : completely volatilise without having any residue.

Ignition Test : Produce yellow sooty flame, i.e. the sample is either aromatic compound or chloroform (C:H ≈ 1:1).

Miscibility with water : The sample is immiscible with water or dil. HCl.

Preliminary Conclusion : Since the sample is colourless liquid, neutral to litmus, immiscible with water and dil. HCl, so it may be one of the following liquid samples:

(i) Benzaldehyde
(ii) Nitrobenzene
(iii) Chloroform

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or liquid but miscible with dil.HCl (like aniline or dimethylaniline). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. Brady's Test : To an alcoholic solution of the sample, Brady's reagent (2-3 ml) and a drop of conc. H_2SO_4 is added. Warmed and cooled if necessary.	No characteristic orange/yellow ppt. obtained.	Benzaldehyde absent.
2. Malachite Green test : Little of the sample is heated in a dry test tube with few drops of *N,N*-dimethylaniline and a bead of anhydrous $ZnCl_2$(solid). After cooling acetic acid and PbO_2 is added to it, shaken well and then conc. HCl is added to it.	No intense green colour is developed.	Benzaldehyde absent.

3. Reduction and the dye test : Little of the sample + conc. HCl (3-5 ml) +Zn-dust (pinch by pinch), warmed and filtered. Filtrate cooled + cold dil. $NaNO_2$ solution dropwise. Now this solution is added to cold alkaline solution of β-naphthol.	No characteristic red or orange dye formed.	Nitrobenzene absent.
4. Little of the sample is boiled with conc. NaOH solution.	No darkening of colour took place.	Absence of nitrobenzene.
5. **Hydrolysis Test :** Little of the sample is boiled with an excess of aq. KOH solution, now it is acidified with HNO_3 and to it, $AgNO_3$ solution is added.	A curdy white ppt. is formed which is soluble in dil. NH_4OH but reappears on acidification with HNO_3	May be chloroform.
6. Fehling's Test : Little of the sample is mixed with Fehling's solution and warmed on water bath.	A yellowish red ppt. formed.	Sample may be chloroform.
7. Resorcinol Test : Little of the sample + resorcinol (solid) is taken in test tube or porcelain basin. To it 2-3 ml of conc. NaOH is added and heated.	A brilliant red colour is developed in aq. Layer.	Chloroform present and confirmed.
8. Carbylamine Test : Sample + few drops of aniline +2 ml of ethanolic KOH solution, heated.	An obnoxious smell of carbylamines(phenyl isocyanide) is evolved.	Chloroform present and confirmed.

Conclusion : The supplied sample is chloroform and its structure is $CHCl_3$.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Pale yellow

Odour : Characteristic smell of bitter almonds.

Litmus : The sample is neutral to litmus.

Action of heat : completely volatilise without leaving any residue.

Ignition Test : Produce yellow sooty flame, i.e. the sample is aromatic compound.

Miscibility with water : The sample is immiscible with water and also immiscible with dil. HCl.

Preliminary Conclusion : Since the sample is colourless liquid, neutral to litmus, immiscible with water and dil. HCl, so it may be one of the following liquid samples:

(iv) Benzaldehyde
(v) Nitrobenzene
(vi) Chloroform

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or liquid but miscible with dil.HCl (like aniline or dimethylaniline). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. Carbylamine Test : Sample + few drops of aniline +2 ml of ethanolic KOH solution, heated.	No obnoxious smell of carbylamines(phenyl isocyanide) is evolved.	Chloroform absent.
2. Brady's Test : To an alcoholic solution of the sample, Brady's reagent (2-3 ml) and a drop of conc. H_2SO_4 is added. Warmed and cooled if necessary.	No reddish yellow crystalline ppt. formed.	Benzaldehyde absent.
3. Malachite Green test : Little of the sample is heated in a dry test tube with few drops of *N,N*-dimethylaniline and a bead of anhydrous $ZnCl_2$(solid). After cooling acetic acid and PbO_2 is added to it, shaken well and then conc. HCl is added to it.	No characteristic intense green colour is developed.	Benzaldehyde absent.

4. Little of the sample is boiled with conc. NaOH solution.	Darkening of colour took place.	May be nitrobenzene.
5. Reduction and the diazo coupling test : Little of the sample + conc. HCl (3-5 ml) +Zn-dust (pinch by pinch), warmed and filtered. Filtrate cooled + cold dil. $NaNO_2$ solution dropwise. Now this solution is added to cold alkaline solution of β-naphthol.	Brilliant scarlet red dye formed.	Nitrobenzene present and confirmed.
6. Mulliken Barker Test : A mixture of 5-10 ml of the sample + EOH (5ml) +NH_4Cl(solid) + Zn dust + water(3-4 drops) is boiled 3-4 mins. and filtered. To the filtrate Tollen's reagent is added and warmed on water bath.	A grey / black ppt. formed.	Nitrobenzene present and confirmed.

Conclusion : The given sample is nitrobenzene and its structure is Ph-NO_2.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless (old sample is brown)

Odour : Characteristic aromatic smell.

Litmus : Weakly basic- changes red litmus to blue .

Action of heat : completely volatilise without having any residue.

Ignition Test : Produce yellow sooty flame, i.e. the sample is aromatic compound.

Miscibility with water : The sample is immiscible with water but completely miscible with dil. HCl.

Preliminary Conclusion : Since the sample is colourless liquid, weakly basic to litmus, immiscible with water but completely miscible with dil. HCl, so it may be either aniline or *N,N*-dimethylaniline.

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or water miscible neutral liquid (ethanol, methanol and acetone). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. Little of the sample is dissolved in dil. HCl and to it $K_4[Fe(CN)_6]$ solution is added.	No white ppt. formed.	*N,N*-dimethyl aniline absent.
2. Malachite Green test : Little of the sample is heated in a dry test tube with few drops of benzaldehyde and a bead of anhydrous $ZnCl_2$(solid). After cooling acetic acid and PbO_2 is added to it, shaken well and then conc. HCl is added to it.	No intense green colour is developed.	*N,N*-dimethyl aniline absent.
3. Bleaching powder Test : To dil. HCl solution of sample, few drops of bleaching powder solution is added.	Purple violet colouration appeared.	May be aniline

4. To a mixture of a drop of organic sample and 5-6 drops of conc. H_2SO_4 taken on a spot plate, a drop of $K_2Cr_2O_7$ solution is added and stirred with a glass rod.	An intense blue colour is developed.	May be aniline.
5. Br_2 water is added to a solution of the sample in dil. HCl	Copious white ppt. formed.	May be aniline.
6. Carbylamine Test : Sample + few drops of chloroform +2 ml of ethanolic KOH solution, heated.	An obnoxious smell of carbylamines(phenyl isocyanide) is evolved.	Aniline present and confirmed.
7. Diazo coupling Test: Little of the sample dissolved in dil. HCl, cooled + cold dil. $NaNO_2$ solution dropwise. Now this solution is added to cold alkaline solution of β-naphthol.	A brilliant red dye is formed.	Sample is aniline- it is confirmed.

Conclusion : The given sample is Aniline and its structure is Ph-NH_2.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless (old sample is brown)

Odour : Characteristic bad smell.

Litmus : Weakly basic- changes red litmus to blue .

Action of heat : completely volatilise without having any residue.

Ignition Test : Produce yellow sooty flame, i.e. the sample is aromatic compound.

Miscibility with water : The sample is immiscible with water but completely miscible with dil. HCl.

Preliminary Conclusion : Since the sample is colourless liquid, weakly basic to litmus, immiscible with water but completely miscible with dil. HCl, so it may be either aniline or *N,N*-dimethylaniline.

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or water miscible neutral liquid (ethanol, methanol and acetone). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. **Bleaching powder Test :** To dil. HCl solution of sample, few drops of bleaching powder solution is added.	No Purple violet colouration appeared.	Aniline absent.
2. **Carbylamine Test :** Sample + few drops of chloroform +2 ml of ethanolic KOH solution, heated.	No obnoxious smell of carbylamines(phenyl isocyanide) is evolved.	Aniline absent.
3. Little of the sample is dissolved in dil. HCl and to it $K_4[Fe(CN)_6]$ solution is added.	A white crystalline ppt. formed which is dissolved on boiling.	*N,N*-dimethyl aniline present.
4. To a cold solution of the sample in dil. HCl, a strong solution of $NaNO_2$ is added.	A red colour or a white ppt. is formed. The solution turns green on addition of dil. NaOH to it.	*N,N*-dimethyl aniline present.

5. Diazo coupling Test: Little of the aniline dissolved in dil. HCl, cooled + cold dil. $NaNO_2$ solution dropwise. Now this solution is added to cold solution of sample and allowed to stand.	A rose red colour is formed.	Sample is *N,N*-dimethylaniline- it is confirmed.
6. Malachite Green test : Little of the sample is heated in a dry test tube with few drops of benzaldehyde and a bead of anhydrous $ZnCl_2$(solid). After cooling acetic acid and PbO_2 is added to it, shaken well and then conc. HCl is added to it.	An intense green colour is developed.	*N,N*-dimethyl aniline present and confirmed.

Conclusion : The given sample is *N,N*-dimethyl aniline and its structure is Ph-NMe_2.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless

Odour : Strong pungent odour.

Litmus : The sample is acidic to litmus and turns blue litmus red .

Action of heat : completely volatilise without having any residue.

Ignition Test : Produce blue non sooty flame, i.e. the sample is non aromatic compound.

Miscibility : The sample is freely miscible with water, dil. HCl and dil.NaOH.

Preliminary Conclusion : Since the sample is colourless liquid, weakly acidic to litmus, miscible with water, dil. HCl, and dil. NaOH, so it may be either formic acid or acetic acid.

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or liquid but immiscible with water (e.g. nitrobenzene, chloroform, aniline, N,N-dimethylaniline, benzaldehyde) or water miscible liquid but neutral to litmus (e.g ethanol,methanol and acetone). So these are absent. To identify the sample the following tests are performed further.

Experiment	Observation	Inference
1. Little of the sample is warmed with conc. H_2SO_4	A brisk evolution of carbom monoxide gas took place- the gas burns with a blue flame when ignited.	May be formic acid.
2. Few drops of $FeCl_3$ solution is added to neutral solution of the sample and warmed.	A red colour is developed which is changed to a brown ppt. on warming.	May be formic acid or acetic acid.
3. Few drops of the neutral solution of the organic sample is heated to dryness and then the residue is mixed with equal parts of As_2O_3 and heated strongly.	No characteristic smell of cacodyl oxide is evolved.	Acetic acid absent.
4. **Denige's Test :** Denige's reagent is added to the neutral solution of the sample and boiled.	A white sand like ppt. obtained.	Sample is formic acid.

5. Mercuric Chloride Test: Few drops of neutral solution of the sample warmed with little $HgCl_2$ solution.	White ppt. formed. The ppt. changed to grey on warming with excess of neutral solution of the sample.	Formic acid present and confirmed.
6. Silver mirror Test : Little of the neutral solution of the sample is warmed with $AgNO_3$ solution.	White ppt. formed which blackens on warming.	Sample is formic acid-confirmed.

Conclusion : The given sample is formic acid and its structure is H-COOH.

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless

Odour : Characteristic smell of vinegar.

Litmus : The sample is acidic to litmus and turns blue litmus red .

Action of heat : completely volatilise without leaving any residue.

Ignition Test : Produce blue non sooty flame, i.e. the sample is non aromatic compound.

Miscibility : The sample is freely miscible with water, in all proportions.

Preliminary Conclusion : Since the sample is colourless liquid, acidic to litmus, miscible with water, dil. HCl, and dil. NaOH, so it may be either formic acid or acetic acid.

The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or liquid but immiscible with water (e.g. nitrobenzene, chloroform, aniline, N,N-dimethylaniline, benzaldehyde) or water miscible liquid but neutral to litmus (e.g ethanol,methanol and acetone). So these are absent. To identify the sample the following tests are performed further.

Experiment	Observation	Inference
1. Few drops of $FeCl_3$ solution is added to neutral solution of the sample and warmed.	A red colour is developed which is changed to a brown ppt. on warming.	May be formic acid or acetic acid.
2. Little of the sample is warmed with conc. H_2SO_4	No carbonmonoxide gas is evolved which burns with blue flame.	Formic acid absent.
3. **Denige's Test :** Denige's reagent is added to the neutral solution of the sample and boiled.	No characteristic white sand like ppt. obtained.	Sample is not formic acid- may be acetic acid.
4. **Mercuric Chloride Test:** Few drops of neutral solution of the sample warmed with little $HgCl_2$ solution.	No white or grey ppt. formed.	Sample is not formic acid- may be acetic acid.
5. **Silver mirror Test :** Little of the neutral solution of the sample is warmed with $AgNO_3$ solution.	White ppt. formed which is not changed to black on warming.	Sample is not formic acid- may be acetic acid.

6. Few drops of the neutral solution of the organic sample is heated to dryness and then the residue is mixed with equal parts of As_2O_3 and heated strongly.	A characteristic smell of cacodyl oxide is evolved.	The sample is Acetic acid- ir is confirmed.

Conclusion : The given sample is formic acid and its structure is CH_3-COOH

Physical Characteristics and Preliminary tests :

State : Liquid

Colour : Colourless

Odour : Pleasant ethereal smell

Litmus : The sample is neutral to litmus

Action of heat : completely volatilise without leaving any residue.

Ignition Test : Produce blue non sooty flame, i.e. the sample is not aromatic compound.

Miscibility with water : The sample is freely miscible with water.

Preliminary Conclusion : Since the sample is colourless liquid, miscible with water and neutral to litmus, it may be either ethanol or methanol or acetone. The possibility of other samples are eliminated as either these are solid (e.g. oxalic acid, citric acid, tartaric acid, succinic acid, glucose, cane sugar, resorcinol, benzoic acid, salicylic acid, urea) or water soluble liquid but acidic (formic acid and acetic acid) or liquid but immiscible with water (like benzaldehyde, chloroform, nitrobenzene, aniline or dimethylaniline). So these are absent. For correct identification of the sample the following tests are performed further.

Experiment	Observation	Inference
1. A Cu-spiral is made repeatedly red hot and introduced in 1-2 ml of the sample taken in a test tube. It is divided in two parts. (c) Part 1 + Schiff's reagent, shaken vigorously. (d) Part II + Tollen's reagent,warmed on water bath.	No Pink colour is developed. No Bright silver mirror formed on the inner wall of the test tube.	ethanol or methanol absent. ethanol or methanol absent.
2. Denig's Test : To about 5 ml of aq. Solution of the sample taken in porcelain basin or conical flask, 3-4 ml of dilute $KMnO_4$ solution is added with cooling in ice water. To it few drops of conc. H_2SO_4 is added when a brown colour is developed. This brown color is destroyed by addition of saturated solution of oxalic acid. Now, to it freshly prepared Schiff's reagent is added and allowed to stand with occasional stirring.	No violet colour is developed within 3-5 minutes.	Methanol or ethanol absent.
1ml of sample + solid benzoic acid + conc. H_2SO_4 (3-4drops) taken in a test tube and heated. After cooling it is poured into excess of $NaHCO_3$ solution.	No characteristic sweet smell of ester is obtained.	Absence of methanol or ethanol.
Little of the sample + 2,4-DNP solution, warmd and cooled.	Yellow crystalline ppt. formed.	May be acetone.

Experiment No. 9 : Estimation of urea by hypobromite method.

Principle :

Urea, (H_2NCONH_2), is quantitatively oxidised to liberate nitrogen gas when it is treated with a measured excess of standardised alkaline solution of hypobromite (OBr^-) :

$$CO(NH_2)_2 + 3\,OBr^- + 2\,OH^- = N_2 + CO_3^{2-} + 3\,Br^-$$

$$\therefore CO(NH_2)_2 \equiv 3OBr^-$$

Unreacted hypobromite may be estimated by allowing it to react with an excess of KI in presence of dil. H_2SO_4, when I_2 is liberated. The liberated I_2 is then back titrated with standard thiosulfate solution using starch as indicator.

$$OBr^- + 2I^- + 2\,H^+ = I_2 + Br^- + H_2O$$

$$I_2 + 2\,S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

$$\therefore OBr^- \equiv I_2 \equiv 2S_2O_3^{2-}$$

$$\therefore CO(NH_2)_2 \equiv 3\,OBr^- \equiv 3\,I_2 \equiv 6\,S_2O_3^{2-}$$

or, $S_2O_3^{2-}$ $\equiv$ 1 equivalent of $Na_2S_2O_3 \equiv (1/6)\,CO(NH_2)_2 \equiv \left(\frac{60}{6}\right)$ g. of urea

$\therefore$ 1000 ml of (N) $S_2O_3^{2-}$ solution $\equiv$ 10 g. of urea

Hypobromite is unstable when prepared directly from bromine and alkali. It is conveniently produced *in situ* by adding an excess of bromide to a solution of hypochlorite.

$$OCl^- + Br^- = OBr^- + Cl^-$$

$$\therefore OBr^- \equiv OCl^-$$

Chemicals required :

a) Standard ((N/20) $K_2Cr_2O_7$ solution : To be prepared by acurate weighing. Weight out ~ 0.6-0.7 g (w) of A.R. $K_2Cr_2O_7$ in a 250 ml volumetric flask, dissolve in distilled water, make upto the mark and mix uniformly. Strength = $\left(\frac{w}{0.6129}\right)$ (N/20)

b) (~N/20) thiosulfate solution : Dissolve ~ 3 g. of $Na_2S_2O_3.5H_2O$ in distilled water and dilute to 250 ml, mix uniformly.

c) (~N/20) Calcium hypochlorite solution.

d) KBr

e) KI

f) 1% Starch solution

g) Sample urea solution : ~ 0.5 to 1.0 g. lit^{-1} in distilled water.

Procedure :

1. (a). Preparation of (~N/20) calcium hypochlorite solution

Depending upon the amount of available chlorine, take 1-2 g. of commercial sample of calcium hypochlorite (bleaching powder) and 100 ml of distilled water in a 250 ml conical flask and shake thoroughly. Filter the slury through a Whatman No. 1 filter paper to remove iron oxide, excess of calcium hydroxide and any other insoluble material in the commercial product. Dilute the filtrate to 250 ml with distilled water. Formation of turbidity on standing due to the precipitation of calcium carbonate, is of no consequence. The standard solution of hypochlorite should be preserved in dark coloured glass stoppered bottle protected from light.

Hypochlorite is a powerful oxidising agent in neutral or alkaline medium.

$$OCl^- + H_2O + 2e \rightarrow 2OH^- + Cl^- \qquad E^\circ = 0.89 \text{ volt.}$$

$\therefore (OCl^-/2)$ = 1 equivalent of OCl^-

(b) (~ N/20) *hypobromite solution :*

A hypobromite solution of known concentration may be prepared extemporaneously by adding an excess potassium bromide to a standard solution of hypochlorite :

$$OCl^- + Br^- \text{ (excess)} \rightarrow OBr^- + Cl^-$$

$\therefore OBr^- \equiv OCl^-$

Hypobromite is also a powerful oxidising agent in neutral or alkaline medium.

$$OBr^- + H_2O + 2e \rightarrow 2OH^- + Br^- \qquad E^\circ = 0.76 \text{ volt}$$

$\therefore (OBr^-/2) \equiv$ 1 equivalent of OBr^-

In many cases hypobromite reacts much faster than hypochlorite.

2. *Standardisation of thiosulfate solution :*

Take an aliquot of 25 ml of standard (N/20) $K_2Cr_2O_7$ in a 500 ml conical flask, add 25 ml of 4(N) H_2SO_4 and 2 g. of KI. Cover the flask and keep in dark for 2-3 minutes. Dilute to 200 ml with distilled water and titrate with the (~ N/20) thiosulfate solution till a pale yellow (straw) colour appears in the solution. Add 2 ml of starch indicator, the solution turns deep blue. Continue titration with the thiosulfate solution till the blue colour is discharged and a bright green colour appears. (Titre = V_1).

3. *Standardisation of hypochlorite solution :*

Take an aliquot of 25 ml of the (~ N/20) hypochlorite solution in a 500 ml conical flask, add 25 ml of 4(N) H_2SO_4 and 2 g. of KI. Cover the flask and keep the solution in dark for 2-3 minutes. Dilute to 200 ml with distilled water, titrate with the standard (~ N/20) thiosulfate solution till a pale yellow (straw) colour appears in the solution. Add 2 ml of starch indicator, the solution turns deep blue. Continue titration with the thiosulfate solution till the blue colour is just discharged (Titre = V_2).

$$OCl^- + 2H^+ + 2e \rightarrow H_2O + Cl^-$$

$$\therefore (OCl^-/2) = 1 \text{ equivalent of } OCl^-$$

$$OCl^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

$$OCl^- \equiv I_2 \equiv 2S_2O_3^{2-}$$

$$\therefore (S_2O_3^{2-}) \equiv I \equiv (OCl^-/2)$$

$$\therefore 1000 \text{ ml of (N) } S_2O_3^{2-} \equiv 1000 \text{ ml of (N) } OCl^-$$

4. *Estimation of urea :*

Take an aliquot of 25 ml of the sample urea solution in a 500 ml conical flask. Add 2 g. of KBr and 0.5 g. of $NaHCO_3$ and shake to dissolve the salts. Add a measured excess (25/50/75 ml or 25 $\times$ x ml) of the standard (N/20) hypochlorite solution using a burette till a permanent yellow colour, (due to Br_2) indicating an excess of hypobromite, persists in the solution. Cover the flask and allow to stand for 5 minutes.

Add 10 ml of 6(N) H_2SO_4 (slowly to avoid vigorous effervescence)and then 1 g. of KI. Cover the flask and allow to stand in dark for 2-3 minutes. Dilute to 200 ml with distilled water (to adjust acidity $\leq$ 0.5 (N)) and finally titrate the liberated iodine with the standard (~N/20) thiosulfate solution till a straw (pale yellow) colour appears. Add 2 ml of starch indicator, the solution becomes deep blue. Continue titration with the thiosulfate solution till the blue colour is just discharged (Titre = V_3).

5. Calculate the total quantity of urea present in the sample.

Calculation :

$$\text{Strength of standard } K_2Cr_2O_7 \text{ solution} = \left(\frac{w}{0.6129}\right)\left(N/20\right)$$

$\because$ 25 ml of standard $\left(\frac{w}{0.6129}\right)\left(N/20\right) K_2Cr_2O_7$

$\equiv V_1$ ml of thiosulfate solution

$$\therefore \text{Strength of thiosulfate solution} = \left(\frac{w \times 25}{0.6129 \times V_1}\right)\left(N/20\right)$$

$\because$ 25 ml of hypochlorite solution = V_2 ml of thiosulfate solution

$\therefore$ $(25 \times x)$ ml of hypochlorite solution

$\equiv x.\ V_2$ ml of thiosulfate solution

Excess hypochlorite $\equiv V_3$ ml of thiosulfate solution

$\therefore$ Hypochlorite (i.e., hypobromite) consumed by 25 ml urea solution

$$\equiv (x.V_2 - V_3)\text{ml of}\left(\frac{w \times 25}{0.6129 \times V_1}\right)\left(N/20\right) \text{ thiosulfate solution}$$

$\because$ 1000 ml of (N) thiosulfate $\equiv$ 10 g. of urea

$$\therefore (x.V_2 - V_3)\text{ml of}\left(\frac{w \times 25}{0.6129 \times V_1}\right)\left(N/20\right) \text{ thiosulfate}$$

$$\equiv \frac{10 \times 25\,w}{1000 \times 0.6129 \times 20} \times \left(\frac{x V_2 - V_3}{V_1}\right) \text{g. of urea,}$$

$\equiv$ 25ml of sample urea solution

$$\therefore \text{Strength of urea solution} = \frac{10.w}{0.6129 \times 20}\left(\frac{x V_2 - V_3}{V_1}\right) \text{g.lit}^{-1}$$

$$= 0.8158 \times \left(\frac{x V_2 - V_3}{V_1}\right) \text{g.lit}^{-1}$$

b) (~ N/20) I_2 in KI solution : Dissolve ~ 1.6 g. of iodine in a solution of 2 g. of KI and dissolved in 20 ml of distilled water and dilute to 250 ml with distilled water.

c) (~ N/20) Thiosulfate solution : Dissolve ~ 3 g. of $Na_2S_2O_3.5H_2O$ in distilled water, dilute to ~ 250 ml and mix uniformly.

d) 10% KI solution.

e) 1% Starch solution.

f) Sample solution :

(i) Vitamin-C tablet may be used for estimation. Known weight of the tablets may be dissolved in water in a volumetric flask (100 ml or 250 ml), diluted upto the mark and shaken to mix uniformly.

(ii) Ascorbic acid solution of known strength : Dissolve ~1 g. of ascorbic acid in distilled water and dilute to 250 ml in a volumetric flask.

Procedure :

1. Standardisation of thiosulfate solution against standard (N/20) $K_2Cr_2O_7$ solution:

Pipette out 25ml of standard (N/20) $K_2Cr_2O_7$ solution in a 500ml conical flask, add 25ml of 4(N) H_2SO_4, and 10 ml of 10% KI solution, cover the flask and allow to stand in the dark for 2-3 minutes. Dilute with 150 ml of distilled water to adjust the acidity ~ 0.5N and titrate the liberated iodine with the thiosulfate solution till the solution assumes a pale yellow colour. Add 2 ml of 1% starch solution. The solution turns intense blue. Continue the titration till the blue colour is just discharged and a bright green colour appears (titre = V_1 ml).

2. Standardisation of iodine solution against standard thiosulfate solution:

Take an aliquot of 25 ml of the (~ N/20) iodine solution in a 500ml conical flask, dilute to 100 ml with distilled water and titrate with the standard (~ N/20) thiosulfate solution till the solution assumes a pale yellow colour. Add 2 ml of 1% starch solution and continue the titration until the blue colour is just discharged. (titre = V_2 ml).

3. Estimation of vitamin- C solution :

Pipette out 25 ml of the diluted vitamin – C solution in a 500 ml conical flask, dilute with 25 ml of distilled water. Add 1 ml of 4(N) H_2SO_4 to adjust the acidity $\leq$ 0.1 (N). Add a measured excess (25/50/75 ml say 25 $\times$ x ml) of standard (~ N/20) iodine solution using a burette so that the iodine colour persists in the solution, allow to stand for 30 seconds. Add 2 ml of 1% starch indicator, the solution turns blue. Titrate quickly with the standardised (~ N/20) thiosulfate solution till the blue colour is just discharged. (titre = V_3 ml)

3. Calculate total quantity of vitamin- C in the sample.

Calculation :

Strength of standard $K_2Cr_2O_7$ solution $= (w / 0.6129)\ (N/20)$

25 ml of $(w / 0.6129)\ (N/20)\ K_2Cr_2O_7 \equiv$ Iodine $\equiv V_1$ ml thiosulfate solution

$\therefore$ Strength of thiosulfate solution $\equiv (25 \times w) / (V_1 \times 0.6129)\ (N/20)$

25 ml of Iodine solution $\equiv V_2$ ml thiosulfate solution

$\therefore$ $(25 \times x)$ ml iodine solution $\equiv x \times V_2$ ml thiosulfate solution

$(25 \times x)$ Iodine solution $\equiv$ (25 ml of Vitamin C solution + V_3 ml of thiosulfate solution)

$\therefore$ 25 ml of Vitamin C solution $\equiv (x \times V_2 - V_3)$ ml of thiosulfate solution

$\because$ 1 ml of (N) thiosulfate solution $\equiv$ 88.06 mg of Vitamin C

$\therefore$ 25 ml of vitamin C solution

$\equiv (x \times V_2 - V_3)$ ml of $(25 \times w) / (V_1 \times 0.6129)\ (N/20)$ thiosulfate solution

$$\equiv \frac{88.06 \times (x \times V_2 - V_3) \times 25 \times w}{V_1 \times 0.6129 \times 20} \text{ mg. of vitamin C}$$

$\therefore$ 1 ml of Vitamin C solution

$$\equiv \frac{88.06 \times (x \times V_2 - V_3) \times 25 \times w}{V_1 \times 0.6129 \times 20 \times 25} \text{ mg. of vitamin C}$$

$\therefore$ Strength of Vitamin C solution

$$= \left(\frac{88.06 \times 1000}{0.6129 \times 20}\right) \times \left(\frac{x V_2 - V_3}{V_1}\right) \text{ mg.lit}^{-1}.$$

$$= \left(\frac{88.06 \times 100}{0.6129 \times 20}\right) \times \left(\frac{x V_2 - V_3}{V_1}\right) \text{ mg.\%}$$

Estimation of acetic acid in commercial vinegar

Experiment No. 15 : Estimation of acetic acid in commercial vinegar

Principle :

When acetic acid (CH_3COOH) is titrated with a strong base such as sodium hydroxide, sodium acetate (CH_3COONa) is produced :

$$CH_3COOH + NaOH = CH_3COONa + H_2O \quad \ldots\ldots\ldots \quad (1)$$

$$\therefore [NaOH] \equiv [CH_3COOH]$$

i.e., 1000 ml of (N) NaOH $\equiv$ 1000 ml of (N) acetic acid.

At the equivalence point, the solution will contain sodium acetate. Sodium ion (Na^+) is neutral. Acetate ion (CH_3COO^-), being the conjugate base of a weak acid, is a strong base and gives an alkaline reaction in water to produce unionised acetic acid molecule and equivalent amount of alkali (OH^-) is released :

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \quad \ldots \ldots (2)$$

$\therefore$ at equilibrium, $[CH_3COOH] = [OH^-]$

pH of such a solution will be given by

$$pH = \tfrac{1}{2} pK_w + \tfrac{1}{2} pK_a + \tfrac{1}{2} \log c \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where, $K_w = [H^+] \times [OH^-]$ = ionic product of water = 10^{-14} at 25°C,

K_a = ionisation constant of acetic acid (1.8×10^{-5} at 25°C)

and c = molar concentration of acetate ion assuming no change of volume.

Thus, pH of (N/20) (i.e., 0.05 M) solution of sodium acetate will be equal to :

$$pH = \tfrac{1}{2}.(14) + \tfrac{1}{2}(4.74) + \tfrac{1}{2} \log (0.05) = 8.72$$

So, phenolphthalein ($pK_{In} = 9.6$) will be a suitable indicator for this titration.

Chemicals required :

1. Standard (N/20) oxalic acid solution.
2. ~ (N/20) Sodium hydroxide solution.
3. Phenolphthalein indicator solution.
4. Sample vinegar solution.

Procedure :

1. Transfer 10 ml of the sample vinegar solution using a burette into a 250 ml volumetric flask, dilute to 250 ml and shake to mix uniformly.
2. Prepare 250 ml of standard (N/20) oxalic solution by accurate weighing.
3. Standardise the ~ (N/20) sodium hydroxide solution by titrating the standard (N/20) oxalic acid solution with it using phenolphthalein indicator (see Ch. – 2).
4. Take an aliquot of 25 ml of the prepared solution of the vinegar sample in a 250 ml conical flask, add 25 ml of distilled water, 2 – 3 drops of phenolphthalein indicator and titrate the mixture with the standard (N/20) sodium hydroxide up to a pink-red end point.

5. Calculate the amount of acetic acid in g/lit. of the vinegar sample.

Calculation :

Let, weight of oxalic acid in 250 ml solution = w g

∴ Strength of oxalic acid solution = (w/0.7879) (N/20)

Let, 25 ml of standard oxalic acid ≡ V_1 ml of NaOH solution.

∴ Strength of NaOH solution = $\left(\frac{25.w}{0.7879.V_1}\right)(N/20)$

Let, 25 ml of diluted solution of vinegar sample ≡ V_2 ml of standard NaOH solution.

∴ Strength of dilute vinegar solution

$$= \frac{V_2 \times 25 \times w}{25 \times V_1 \times 0.7879} \quad (N/20)$$

$$= \frac{V_2 \times w}{V_1 \times 0.7879} \quad (N/20)$$

∴ Strength of original solution of vinegar

$$= 10 \times \frac{V_2 \times w}{V_1 \times 0.7879} \times (N/20)$$

$$= \left(\frac{V_2 \times w}{V_1 \times 0.7879 \times 2}\right) (N)$$

Since the formula weight of acetic acid (CH_3COOH) is 60 = its equivalent weight

∴ strength of acetic acid in g. / lit.

$$= \left(\frac{60}{0.7879 \times 2}\right) \cdot \left(\frac{wV_2}{V_1}\right) \text{ g./lit}$$

$$= 38.076 \left(\frac{wV_2}{V_1}\right) \text{ g./lit}$$

Experiment No. 10 : Estimation of aromatic amines (aniline) by bromination method.

Principle :

Aromatic amines may be estimated by bromination method by treating a known volume of the amine solution in dilute HCl with a measured excess of standard $KBrO_3$ - KBr mixture (brominating agent). Bromine generated *in situ* by the reaction of BrO_3^- with Br^- in acid medium reacts quantitatively with the amine to form the corresponding bromo derivatives which precipitate. When aniline, $C_6H_5NH_2$, is treated with a measured excess of bromate-bromide mixture in dil. HCl medium, 2,4, 6-tribromoaniline ($C_6H_2(Br_3)NH_2$) is quantitatively formed and precipitated. The unreacted bromine is then made to react with an excess KI and the I_2 that is liberated is titrated with a standard sodium thiosulfate solution using starch indicator. The thiosulfate solution is standardised against the same standard $KBrO_3$ – KBr mixture. The difference of these two titre values gives the amount of bromine reacted with the amine (aniline) and thus the amine (aniline) is estimated.

$$BrO_3^- + 6H^+ + 5Br^- = 3\,Br_2 + 3H_2O$$

$$\therefore BrO_3^- \equiv 3Br_2 \equiv 6Br$$

$$C_6H_5NH_2 + 3\,Br_2 = C_6H_2(Br)_3NH_2 + 3\,HBr$$

$$\therefore C_6H_5NH_2 \equiv 3Br_2 \equiv 6Br$$

$$Br_2 + 2\,I^- = I_2 + 2\,Br^-$$

$$\therefore Br_2 \equiv 2Br \equiv I_2 \equiv 2\,I$$

$$2\,S_2O_3^{2-} + I_2 = 2\,I^- + S_4O_6^{2-}$$

$$\therefore 2S_2O_3^{2-} \equiv I_2 \equiv 2\,I$$

$$\therefore BrO_3^- \equiv 3\,Br_2 \equiv C_6H_5NH_2 \equiv 3\,I_2 = 6\,S_2O_3^{2-}$$

$$\therefore S_2O_3^{2-} \equiv 1 \text{ equivalent of } Na_2S_2O_3 \equiv (1/6)\,C_6H_5NH_2$$

(Since, $2\,S_2O_3^{2-} - 2e \rightarrow S_4O_6^{2-}$)

$\therefore$ 1000 ml of (N) $S_2O_3^{2-}$ solution $\equiv$ (93.066/6) g. = 15.511 g of aniline.

In acid solution, BrO_3^- acts as an oxidant according to,

$$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O$$

$$\therefore \text{The equivalent weight of } KBrO_3 = \left(\frac{KBrO_3}{6}\right) = (167/6) = 27.8334$$

$\therefore$ 250 ml (N/20) $KBrO_3$ solution $\equiv$ 0.3479 g. of $KBrO_3$.

Chemicals required :

a) Aromatic amine (aniline) : Stock solution may be prepared by dissolving 3.5 – 4 g (3-4 ml) of freshly distilled aniline in 150 ml of 1:1 HCl solution and finally diluting to one litre with distilled water (acidity ~ 0.8 – 0.9 N).

20-25 ml of this stock solution may be diluted to 100 ml in a volumetric flask. 25 ml of this diluted solution may be used for titration. (acidity ~ 0.2 N).

b) Standard (N/20) $KBrO_3$ – KBr mixture : Weigh out accurately ~ 0.4 g. (w) of (A.R.) $KBrO_3$ (exactly; 0.3479 g) and add ~ 5 g. of (A.R.) KBr in a 250 ml volumetric flask, dissolve in distilled water and dilute upto the mark with distilled water. Strength : (w/0.3479) (N/20).

c) 10% KI solution :

d) (N/20) Sodium thiosulfate solution : Dissolve ~ 3-4 g. of $Na_2S_2O_3.5H_2O$ in distilled water and dilute to 250 ml.

e) 1% Starch solution :

Procedure :

1. *Standardisation of sodium thiosulfate solution against standard $KBrO_3$ - KBr mixture :*

Pipette out 25 ml of standard (N/20) $KBrO_3$ – KBr mixture in a 500ml conical flask. Add 10 ml of 10% KI solution and then 5 ml of concentrated (A.R.) HCl to adjust the acidity of the resulting solution to ~1.5 N. Cover the flask and keep in dark for 2-3 minutes. Dilute with 100 ml of water to lower the acidity below ~0.5N. Titrate the liberated I_2 with the (~ N/20) thiosulfate till the colour of the solution turns pale yellow (straw colour). Add 2 ml of starch indicator, the solution becomes intense blue. Continue titration with the thiosulfate solution till the blue colour is just discharged. (titre = V_1).

2. *Estimation of amine (aniline) :*

Transfer the sample amine solution into a 100 ml volumetric flask and make up to the mark with distilled water.

Take an aliquot of 25 ml of the diluted amine solution in to a 500ml conical flask using a burette. Add 10-12 ml concentrated HCl to maintain 1.5 (N) acidity during the subsequent reaction. Add a measured excess (25/50/75 ml say $25 \times x$) ml) of standard (N/20) $KBrO_3$ – KBr mixture, till a permanent yellow colour due to free Br_2 (indicating an excess of the BrO^- - Br^-), persists in the solution. Cover the flask with a watch glass, shake and allow to stand at room temperature in the dark for 5-10 minutes with occasional shaking. Add 10ml of 10% KI solution, dilute with 150 ml of distilled water to adjust the acidity ~0.5N. Titrate the liberated I_2 with standard (N/20) thiosulfate solution as usual using starch

indicator near the end point. Continue titration till the blue colour is discharged completely. (Shake thoroughly to disorbe any I_2 adsorbed by the precipitate of the bromo derivative). (titre = V_2 ml).

3. Calculate the total quantity of aniline (amine) present in the sample solution.

Calculation :

$$\text{Strength of } KBrO_3 - KBr \text{ mixture} = \left(\frac{w}{0.3479}\right)\left(\frac{N}{20}\right)$$

25 ml of $KBrO_3 - KBr$ mixture $\equiv V_1$ ml thiosulfate solution

$$\therefore \text{ Strength of thiosulfate solution} = \left(\frac{25w}{0.3479 \times V_1}\right)\left(\frac{N}{20}\right)$$

$\therefore$ $(25 \times x)$ ml of $KBrO_3$-KBr mixture $= x\,V_1$ ml of thiosulfate solution.

$\therefore$ $KBrO_3 - KBr$ mixture consumed by 25 ml of aniline solution

$$\equiv (V_1 x - V_2) \text{ ml of } \left(\frac{25.w}{0.3479 \times V_1}\right) (N/20) \text{ thiosulfate solution}$$

$$\equiv \frac{25.w(V_1 x - V_2)}{0.3479 \times V_1 \times 20} \text{ ml of (N) thiosulfate solution}$$

$$\equiv \left(\frac{0.01551 \times 25}{0.3479 \times 20}\right)\left(\frac{w(V_1 x - V_2)}{V_1}\right) \text{ g. of aniline}$$

($\because$ 1000 ml of (N) thiosulphate solution $\equiv$ 15.511 g. of aniline.)

$\therefore$ Amount of aniline in the sample solution

$$\equiv \left(\frac{0.015511 \times 25 \times 100}{0.3479 \times 20 \times 25}\right) \times \left[\frac{w(V_1 x - V_2)}{V_1}\right] \text{ g.}$$

$$\equiv \left(\frac{0.015511 \times 5}{0.3479}\right) \times \left[\frac{w(V_1 x - V_2)}{V_1}\right] \text{ g.}$$

$$= 0.2229 \times \left[\frac{w(V_1 x - V_2)}{V_1}\right] \text{ g.}$$

Experiment No. 12 : Estimation of formaldehyde (formalin)

Principle :

Formaldehyde (formalin), HCHO, is estimated by iodimetric method. When a known volume of formalin solution is allowed to react with a measured excess of iodine (I_2) solution in weakly alkaline medium, formaldehyde is quantitatively oxidised to formate ($HCOO^-$) ion according to,

$$HCHO + I_2 + 3NaOH = 2NaI + 2H_2O + HCOO^- Na^+$$

$$\therefore \quad I_2 \equiv HCHO$$

By back titrating the excess iodine with a standard solution of sodium thiosulfate in weakly acidic medium, it is possible to determine the quantity of I_2 that has reacted with HCHO, hence the quantity of HCHO present in the formalin solution can be found out from the difference in the titre values. Thiosulfate ($S_2O_3^{2-}$) is oxidised by I_2 to tetrathionate ($S_4O_6^{2-}$) according to,

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

$$\therefore \quad I_2 \equiv 2S_2O_3^{2-}$$

$$\therefore \quad 2S_2O_3^{2-} \equiv I_2 \equiv HCHO$$

$\therefore$ 2000 ml of (N) thiosulfate $\equiv$ 30 g. of HCHO

$\therefore$ 1 ml of (N) thiosulfate $\equiv$ (30/2000) g. $\equiv$ 0.015 g. of HCHO.

Chemicals required :

1. $K_2Cr_2O_7$ (A.R.).
2. Sodium thiosulfate solution.
3. (~ N/20) Iodine solution (100 ml). Dissolve 2 g. of iodate free potassium iodide in 20 ml of distilled water taken in a stoppered 250 ml conical flask. Transfer 0.6 – 0.8 g of resublimed iodine in to it and shake well to dissolve completely. Cool to room temperature and dilute to 100 ml with distilled water.
4. 5% NaOH solution (~ 1.25 N) 100 ml
5. (i) 4(N) HCl solution 100 ml

   (ii) 5% HCl solution (~ 0.5 N) 100 ml
6. Starch indicator solution.

Procedure :

1. Prepare 25 ml of a standard (N/20) $K_2Cr_2O_7$ by accurate weighing (~0.6 – 0.8 g/ 250 ml)

2. Prepare 200 ml of (~ N/20) sodium thiosulfate solution.

3. Standardise the sodium thiosulfate solution against standard (N/20) $K_2Cr_2O_7$ solution.

Take an aliquot of 25 ml of standard (N/20) $K_2Cr_2O_7$ solution in a 500 ml conical flask, add 25 ml of 4(N) HCl, 2 g. of KI, stoper the flask and allow to stand in dark for ~ 2 – 3 minutes. Dilute with 150 ml of distilled water to adjust the acidity to $\leq$ 0.5(N) and titrate with the (~ N/20) thiosulfate solution as usual using starch indicator near the end point. Colour change at the end point is from blue to bright green (titre = V_1 ml).

4. Standardization of I_2 solution.

Take an aliquot of 25 ml of the I_2 solution in a 500 ml conical flask, add 25 ml of the 5% HCl solution and titrate with standard (N/20) thiosulfate solution using starch indicator as usual. Colour change at the end point is from blue to colourless. (titre = V_2 ml)

5. Estimation of formalin :

(a) Transfer quantitatively a known volume (V ml) of the sample formalin solution into a 100 ml volumetric flask and make up to the mark with distilled water and mix uniformly.

(b) Take an aliquot of 25 ml of the diluted solution of formalin into a 500 ml conical flask, add a measured excess (25 / 50 / 75 ml i.e., 25 $\times$ x ml, as required) of standard (N/20) I_2 solution and drops of 5% NaOH solution till the solution becomes light yellow and the yellow colour persists even the mixture is kept for 15 minutes. Yellow colour may disappear if the NaOH solution is added in excess.

After standing for 15 minutes add 15 ml of 5% HCl solution and titrate the liberated I_2 with standard (N/20) thiosulfate solution using starch indicator as usual. Colour change at the end point is from blue to colourless. (titre = V_3 ml)

6. Calculate the % of HCHO in sample formation solution.

Calculation :

$$\text{Strength } K_2Cr_2O_7 \text{ solution} = \frac{w}{0.6129}(N/20)$$

where, w = wt. of $K_2Cr_2O_7$ in 250 ml solution.

25 ml of standard (w / 0.6129) (N/20) $K_2Cr_2O_7 \equiv V_1$ ml of thiosulfate solution.

$\therefore$ Strength of thiosulfate solution $= \left(\frac{25 \times w}{V_1 \times 0.6129}\right)$ (N/20)

25 ml of I_2 solution $\equiv$ V_2 ml of thiosulfate solution

$\therefore$ $(25 \times x)$ ml of I_2 solution

$\equiv$ $(V_2 \times x)$ ml of thiosulfate solution

$\equiv$ V_3 ml of thiosulfate solution + 25 ml of diluted formalin solution.

$\therefore$ 25 ml of sample of diluted formalin solution

$\equiv (V_2 x - V_3)$ ml of $\left(\frac{25 \times w}{V_1 \times 0.6129}\right)$ (N/20) thiosulfate solution.

$\equiv \left(\frac{25}{0.6129 \times 20}\right) \times \frac{w\,(V_2 x - V_3)}{V_1}$ ml of (N) thiosulfate solution.

$\equiv \left(\frac{25 \times 0.015}{0.6129 \times 20}\right) \times \frac{w\,(V_2 x - V_3)}{V_1}$ g of HCHO

$\therefore$ Total formaldehyde in 100 ml of the diluted formalin solution

$\equiv \left(\frac{25 \times 0.015 \times 100}{0.6129 \times 20 \times 25}\right) \times \frac{w\,(V_2 x - V_3)}{V_1}$ g of HCHO in V ml of the sample

$= 0.1224 \times \frac{w(V_2 x - V_3)}{V_1}$ g. of HCHO

$\therefore$ Strength of the sample formalin solution $= 12.24 \times [w\,(V_2 x - V_3)/V.V_1]$ %.

BIBLIOGRAPHY

1. University Hand Book of Undergraduate Chemistry Experiments, edited by Mukherjee, G. N., University of Calcutta, 2003.
2. Das, S. C., Chakraborty, S. B., Practical Chemistry.
3. Mukherjee, K. S. Text book on Practical Chemistry, New Oriental Book Agency.
4. Ghosal, Mahapatra and Nad, An Advanced Course in Practical Chemistry, New Central Book Agency.
5. Palit, S.R., Practical Physical Chemistry Science Book Agency.
6. Mukherjee, N.G., Selected Experiments in Physical Chemistry J. N. Ghose and Sons.
7. Dutta, S.K., Physical Chemistry Experiments Bharati Book Stall.
8. Vogel, A. I. Elementary Practical Organic Chemistry, Part 2: Qualitative Organic Analysis, CBS Publishers and Distributors.
9. Vogel, A.I., Tatchell, A.R., Furnis, B.S., Hannaford, A.J. & Smith, P.W.G., Textbook of Practical Organic Chemistry, Prentice-Hall, 5th edition, 1996.
10. Mann, F.G. and Saunders, B.C. Practical Organic Chemistry Orient-Longman, 1960.
11. Viswanathan, B., Raghavan, P.S. Practical Physical Chemistry Viva Books (2009).
12. Mendham, J., A. I. Vogel's Quantitative Chemical Analysis 6th Ed., Pearson.
13. Levitt, B. P. edited Findlay's Practical Physical Chemistry Longman Group Ltd.
14. Gurtu, J. N., Kapoor, R., Advanced Experimental Chemistry S. Chand & Co. Ltd.
15. Ahluwalia, V.K. & Aggarwal, R. Comprehensive Practical Organic Chemistry: Preparation and Quantitative Analysis, University Press (2000).
16. Practical Workbook Chemistry (Honours), UGBS, Chemistry, University of Calcutta, 2015.
17. Svehla, G. Vogel's Qualitative Inorganic Analysis, Pearson Education, 2012.
18. Khosla, B. D.; Garg, V. C. & Gulati, A. Senior Practical Physical Chemistry, R. Chand & Co.: New Delhi (2011).
19. Levitt, B. P. edited Findlay's Practical Physical Chemistry Longman Group Ltd.
20. Clarke, H. T., A Handbook of Organic Analysis (Qualitative and Quantitative), Fourth Edition, CBS Publishers and Distributors (2007).

PART – IV:
LABORATORY PRACTICES: PROTOCOLS AND SAFETY

CONTENTS **PAGE**

Laboratory Policies

Laboratory is a common space shared by many students. Hence it is obligatory on each and every student to be responsible for his/her own safety and the safety of his/her classmates. Safety in a laboratory may mean more than just putting on a laboratory apron (lab coat) and appropriate handling of chemicals and instruments/apparatus. For safe conduct of any experiment, every student must follow some routine policies in terms of their personal behaviour, upkeeping of work space, knowledge of chemicals and operation of instruments etc. The following policies must be adhered to while in a lab.

1. Personal safety and safety of co-workers

(a) Lab apron (lab coat) must be worn while working in the lab.
(b) Loosely flowing clothes or synthetic clothes must not be worn during a lab session. Cotton clothes which cover both hands and legs are recommended.
(c) Shoes which cover the foot completely (not slipper or shoes/sandals that expose the toe) must be worn.
(d) Long hair may pose the risk of catching fire; hence the hair must be tied as a bun behind the head.
(e) Safety goggles are a must.
(f) Complete silence must be maintained in the lab.
(g) Any queries must be discussed with the teacher of the class.
(h) Eating or drinking is strictly not allowed in the lab. If thirsty one must thoroughly clean one's hands and then go out of the lab to have water.
(i) Stools must not be kept on the walkway to avoid tumbling of coworkers.
(j) One must not run in the lab.
(k) One must always be aware of people moving around with glassware/chemicals to avoid accidents.
(l) Always use suitable trays for carrying multiple glass apparatus from one lab to the other.
(m) Each person working in the lab is responsible for her own safety and the safety of her lab mates.

2. Work area

(a) It is important to keep the working bench clean and without clutter for safe operations.
(b) Trash must be put in trash bins and not in sink. Filter papers, match sticks etc must not be put into the sink.
(c) Any lighted match stick must be put off completely, allowed to cool and then only disposed off in the trash bins.
(d) Any spills must be immediately wiped off taking necessary precautions. If anything spills on the floor. the laboratory staff must be informed of the same for immediate cleaning.
(e) All necessary apparatus must be picked up from the shelves and replaced once the experiment is complete.
(f) Apparatus that are issued in a particular student's name must be returned on completion of the work.
(g) After completion of the work all apparatus must be returned and the working space cleaned of any litter.
(h) All experiment involving hazardous /flammable/fuming chemicals must be carried out in the fumes hood.
(i) The common instruments such as balances and pH meters must be cleaned for any spills before leaving the work place.

3. Material safety data sheet (MSDS)

(a) It is important to study in advance, the MSDS for the chemicals that one will be using in the lab.
(b) The MSDS gives information about the health, fire, reactivity, environmental hazards, if any, associated with the use of the chemical and how to safely handle the chemical.
(c) The label on the bottle of the chemical also gives information about it. It must be read thoroughly and the risks of handling it to be understood.

4. Use of instruments

(a) Use of any specialized instrument must be done with the help of the teacher and the laboratory staff only.

(b) All such instruments must be handled with great care.

(c) The instruments must be left in the same condition as before. The necessary precautions and handling will be taught by the respective teachers.

5. Accidents

(a) It is never advisable to work all alone in a lab. If a project work is being carried out, the presence of the teacher supervisor is compulsory.

(b) Unless there is a scheduled laboratory class, students should refrain from entering the lab.

(c) Whenever there is any injury with broken glass pieces or any chemical spills on a person, the laboratory staff and the teachers associated with the lab class must immediately be informed.

(d) Necessary first aid must be provided by the laboratory staff and the teachers to the injured student and if required. medical assistance must be provided.

(e) In case of a major accident, the office may also be informed in addition, in which case, a proper vehicle may be arranged for transport of the injured person.

(f) The first aid for the management of injuries with everyday chemicals is the responsibility of the teachers of the department concerned.

STANDARD OPERATING PROCEDURES (SOPs) FOR THE CHEMISTRY LABORATORIES
DEPARTMENT OF CHEMISTRY (UG & PG), JHARGRAM RAJ COLLEGE

SOPs specific to Chemistry Laboratories:

The purpose of this SOP is to provide standard operating procedures for handling of chemicals and apparatus in the Department of Chemistry laboratories. This is in addition to the routine precautions that are followed while working in a chemistry lab. A separate SOP is available for handling of instruments.

1. RESPONSIBILITIES OF THE STUDENTS

All students entering a Chemistry lab or instrument lab are required to:

(a) Adhere to the policies of the college and follow instructions given therein.
(b) Follow the instructions of the teachers during the class.
(c) Always wash up after using chemicals.
(d) Always read the Material Safety Data Sheet about the chemicals prior to use (see Annexure).
(e) Use safety goggles, lab coat while performing any experiment. Use gloves when instructed.
(f) In case of any accident/incident (however big or small), inform the teacher immediately.
(g) Be aware of all emergency procedures.
(h) Do not perform any experiment/reaction without the permission of the teacher.
(i) Do not taste any chemical from the laboratory bottles even though they may seem to be common/harmless such as salt/glucose etc.

2. RESPONSIBILITIES OF TEACHERS

All teachers are required to make sure that:

(a) The students have read the SOP and understood them.
(b) The students are aware of the characteristics of the chemical through the Material Safety Data Sheet and know its safe handling.
(c) The teachers themselves (does they here refer to teachers or students) are aware of the safe handling of each chemical being used in the laboratory.
(d) The students do not violate the safety norms.
(e) Report any safety violation by the any staff/student to the Head of the Department.
(f) Report any major laboratory accident to the TIC immediately and provide medical aid to the injured as soon as possible.

3. RESPONSIBILITIES OF LABORATORY SUPPORT STAFF

All members of the laboratory staff are required to:

(a) Make sure that the work allotted to them is complete and the lab is in proper order.
(b) Be responsible for the general safety of the students and all your colleagues.
(c) Be alert while in the chemistry lab.
(d) Handle chemicals safely.
(e) Understand the meaning of the symbol on the bottle of chemical.
(f) Understand the nature of each chemical used in laboratory and store them accordingly.
(g) Store chemicals properly so as to not result in dangerous reactions/explosions/fire etc.
(h) Store all hazardous chemicals separately.
(i) Act swiftly and help the victim in case of any accident.
(j) Monitor the way students/colleagues handle the chemicals and take necessary/suitable action on violation of safety norms.
(k) Clean up chemical spill immediately taking due care.
(l) Evacuate the students to safety in case of emergency.
(m) Remove any mercury spills immediately.
(n) Do not touch any chemical with bare hands; always use a spatula or a dropper.

(o) Do not to waste chemicals.
(p) Wherever possible, use the left-over solutions for another class.

4. HOUSEKEEPING PRACTICES

A laboratory in the college is a place used by students across many courses. It is therefore, pertinent to follow good housekeeping practices. Here are some tips for maintaining a laboratory a pleasant place to work.

(a) The laboratory must be kept neat and clean at all times.
(b) All apparatus and chemicals must be kept in their designated places.
(c) Working bench must be kept free from unnecessary apparatus, paper, chemicals, waste.
(d) Always a cleaning duster must be kept handy to clean any spills.
(e) All spills must be immediately cleaned up taking necessary precautions.
(f) Laboratory staff may be approached to clean up dangerous spills.
(g) No stools must be left in the path between the working tables.
(h) All paths to exits must be kept unobstructed.
(i) All chemical containers must be labelled for easy identification
(j) Broken glassware must be handled with care.
(k) Clean all your apparatus before putting in the locker or returning at the counter
(l) Clean your work area completely before leaving the lab.
(m) Boss and clamp, wire gauze, tripod stand etc must be returned back to their designated place.
(n) Return bottles of chemicals to their designated place.
(o) All unused (clean) solutions must be returned to the stock from where it was taken.

5. DO'S AND DON'T'S

(a) Do not store food in the laboratory refrigerator. It is for chemicals only.
(b) Do not keep your bags on the working bench. Keep them at the designated places only.
(c) Do not eat or drink in the laboratory.
(d) Do not keep your mobile phone near you while working in a chemistry laboratory.
(e) Do not run around in the laboratory.
(f) Do not bring visitors to the laboratory.
(g) Do not wear flowing dresses while in laboratory. Keep your dupatta/scarf in your bag.
(h) Do not wear synthetic clothes while in laboratory. Wear cotton clothes.
(i) Do not wear shorts while working in the laboratory. Wear full pants/salwar and full sleeve shirts/kurta.
(j) Do not wear a doctor's coat with half sleeve. A lab coat has full sleeves.
(k) Do not wear slippers/sandals while working in the laboratory. Wear shoes.
(l) Do not leave hair open while working in laboratory. Tie it up and make a bun.
(m) Do not throw a burning matchstick in the sink or in the dustbin.
(n) Do not throw unused sodium metal in the dustbin. Consult teacher for proper disposal.

6. ACCIDENT AND INJURY MITIGATION

A. PREVENTION

- Be alert while working in the laboratory.
- Make cautious efforts to prevent accidents.
- Do not point test tubes with boiling liquid towards a co-worker.
- Handle all chemicals with a spatula or a dropper as the case may be.
- Do not allow chemicals to come into contact with your skin or clothing.
- Do not inhale or taste chemicals.
- Do not mix chemicals before understanding their reaction.

B. ROUTES OF EXPOSURE TO CHEMICALS
- Inhalation
- Ingestion
- Absorption

C. SYMPTOMS OF POSSIBLE OVEREXPOSURE
- Eye discomfort
- Breathing difficulty
- Dizziness
- Headache
- Nausea
- Vomiting
- Skin irritation

D. FIRST-AID ON OVER EXPOSURE

If the victim is feeling weak and suffocating, move him/her to fresh air. Seek immediate medical attention. Following are some first-aid measures for specific purposes:

(a) For Chemicals in the Eyes
- Do not rub the eyes.
- Hold eyelids open and flush with water for 15 minutes.
- Be careful not to contaminate the other eye.
- Seek additional medical attention.

(b) For Chemicals on the Skin
- Flush area with lukewarm water for 15 minutes.
- Remove clothing and jewellery from the burn area.
- Seek additional medical attention.

(c) For Chemical Inhalation
- Move victim to fresh air.
- Get immediate medical attention.

(d) For Chemical Ingestion
- Do not induce vomiting unless told by Poison Control.
- Get immediate medical attention.

Annexure: What is a Material Safety Data Sheet?

A Material Safety Data Sheet is a document, specific to a particular chemical, prepared by the chemical manufacturer or importer, describing
- Physical hazards, such as fire and explosion.
- Health hazards, such as signs of exposure.
- Routes of exposure.
- Precautions for safe handling and use.
- Emergency and first-aid procedures.

STANDARD OPERATING PROCEDURES (SOPs) FOR THE INSTRUMENT LABORATORIES
DEPARTMENT OF CHEMISTRY (UG & PG), JHARGRAM RAJ COLLEGE

SOPs specific to Instrument Laboratories:

The purpose of this SOP is to provide standard operating procedures for handling of instruments and apparatus (including the electronic and/or digital balances) in the Department of Chemistry laboratories. This is in addition to the routine precautions that are followed while working in a chemistry lab. A separate SOP is available for handling of chemicals.

7. RESPONSIBILITIES OF THE STUDENTS

(a) Please do not enter the instrument laboratory without the supervision of your teacher.
(b) No instrument/balance should be moved from its place. In case of such a necessity, take the help of the laboratory support staff.
(c) Handle any instrument or weighing balance with extreme care.
(d) Notebooks or bags should not be kept on the working table or the instrument.
(e) Bags must always be put away from the instruments.
(f) Always read the instruction manual or learn from your teacher about how to operate an instrument.
(g) Take care not to spill any chemical on the instrument and clean up immediately if it happens.
(h) Do not weigh any chemical directly on the pan of a balance.
(i) Handle the electrodes which are made of glass with extreme caution.
(j) Follow the guidelines for instrument storage after use.

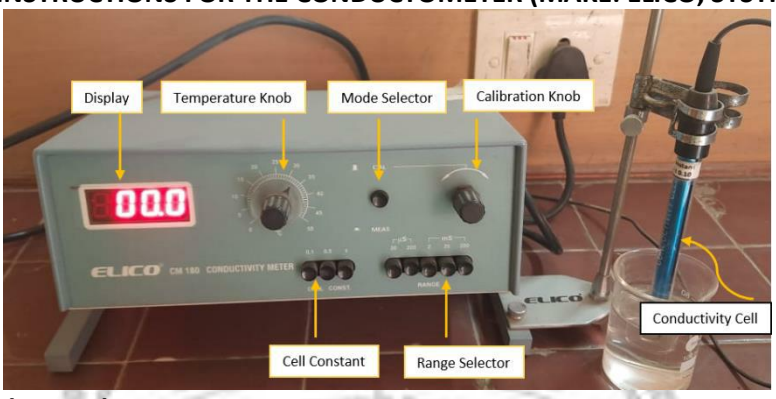
8. RESPONSIBILITIES OF TEACHERS

Teachers are:
(a) Urged to read the instrument's user manual and familiarize themselves with the instrument's operation. They may even discuss with their colleagues.
(b) Urged to monitor the students closely while they are using the instruments to avoid break down of the instruments.
(c) Requested to make small batches of students for using instruments in order to avoid crowding.

9. RESPONSIBILITIES OF LABORATORY SUPPORT STAFF

(a) The lab staff members who have been assigned the duty are accountable for taking care of the instrument lab.
(b) Monitor the use of instruments by the students during the class.
(c) Students should be allowed to enter the lab and use the instruments only in presence of a class teacher/mentor.
(d) No one should be allowed to eat or drink in the instrument lab.
(e) Once the class is over, each instrument must be checked for proper storage and must be switched off.
(f) Any breakage must be immediately entered in the breakage register and the Teacher-in-charge informed about it.
(g) Any malfunctioning of an instrument must be immediately attended to.
(h) It must also be verified that all the electrodes have been dipped in a beaker containing clean distilled water.

USAGE INSTRUCTIONS FOR THE CONDUCTOMETER (MAKE: ELICO, SYSTRONICS)



Components of the Conductometer

(a) **Power switch:** It is located at the back of the instrument. When it is switched on, the display panel in the front glows.

(b) **Control Units of Conductometer:** All other controls are present on the front panel. A brief description of the various controls meant for conductivity measurement is tabulated below:

Temperature knob	With the help of this knob, the temperature can be set to values of 0 to 50 °C. Before any measurement, the temperature of measurement is set to the required value with this control.
Mode selector	This is a toggle switch present on the front panel of the instrument. It has the position marked CAL and READ. This is used to set the instrument either at the CAL (calibration) or READ(read) mode. When the toggle switch is in the depressed position, it is in the READ mode; otherwise, it is in the CAL mode.
CAL mode and the associated CAL knob	After selecting the CAL mode, the instrument is calibrated by rotating the CAL knob in clockwise or anticlockwise direction.
Cell constant	There are three keys for selecting the cell constant viz., $0.1, 0.5, 1$.
Range selector	There are five switches for selecting the range within which the conductance of the sample lies. These are marked $20\ \mu S$, $200\ \mu S$, $2\ mS$, $20\ mS$ and $200\ mS$. When the range selector is at $20\ mS$, the conductometer reads between 2 and $20\ mS$.
Conductivity cell	It consists of two platinized (coated black) platinum electrodes with a cylindrical glass or plastic outer covering which is open at the bottom. This open end is dipped into the solution whose conductance is to be measured. From the top of the cell, emerge two leads which must be connected to the conductometer.

Operating instructions:

(a) Switch on the instrument and give it a warm up time of at least 15 minutes.

(b) Rinse the conductivity cell with the solution whose conductivity is to be measured.

(c) Dip the cell into the test solution, and set the READ/CAL key to the CAL position.

(d) The display must read 1000, irrespective of decimal. If it does not, then using the CAL knob set it to 1000.

(e) Set the temperature at the room temperature value using temperature knob; set the cell constant at 1.

(f) Dip the conductivity cell into a beaker containing the test solution taking care to dip the electrodes completely into the solution.

(g) Shift the READ/CAL key at READ.

(h) Select any one range by pushing the range keys by trial and error so as to obtain a display with maximum decimal points.

(i) The display gives the specific conductance of the solution and since the cell constant is set to 1, it is also the observed conductance.

USAGE INSTRUCTIONS FOR THE pH METER (MAKE: ELICO, SYSTRONICS)

Components of the pH Meter

(a) **Power switch:** This switch is at the front of the instrument. When it is switched on, the display panel in the front glows.

(b) **Control Units of the pH Meter:** All other controls are present on the front panel. A brief description of the various controls meant for pH measurement is tabulated below:

Temperature knob	With the help of this knob, the temperature can be set to values of 0 to 50 °C. Before any measurement, the temperature of measurement is set to the required value with this control.
pH Calibration knob	This knob is used to calibrate the instrument with the given known pH solutions by rotating it clockwise/anticlockwise.
Standby/Read knob	While not in use, the instrument is kept at Standby mode. For readings, it is kept at Read position.
pH/mV knob	This knob is used to choose the display mode as pH or potential, as required.

Operating instructions:

A. Calibration:

The very first step towards measuring the pH of a solution is to calibrate the instrument. The steps of calibration are given below.

(a) Set the temperature to room temperature.

(b) Set the instrument to pH mode by pressing the pH/mV knob. Calibrate the pH-meter using buffer solutions of pH 4.01 (or any suitable buffer) ,7.0, and 9.2 (or any suitable buffer).

(c) Wash the electrode with water, wipe it gently with a soft tissue; rinse it with a buffer of pH 4.01.

(d) Dip it into a fresh buffer solution of pH 4.01.

(e) Swirl the solution and using the pH/mV push-button set the instrument to pH mode.

(f) Similarly using the standby/read push-button, set it to Read mode.

(g) Now note the pH from the display. If it is different from 4.01, then adjust the display to the desired value by rotating the CAL knob.

(h) Bring the instrument to the standby mode, remove the electrode from the buffer, wash it thoroughly with water, dab it gently with a soft tissue, rinse it with a buffer of pH 7.0 and calibrate with this buffer.

(i) Similarly calibrate the electrode with pH 9.2. Repeat the entire procedure of calibration with three buffer solutions at least three times or till the desired pH values are obtained for all the buffers used.

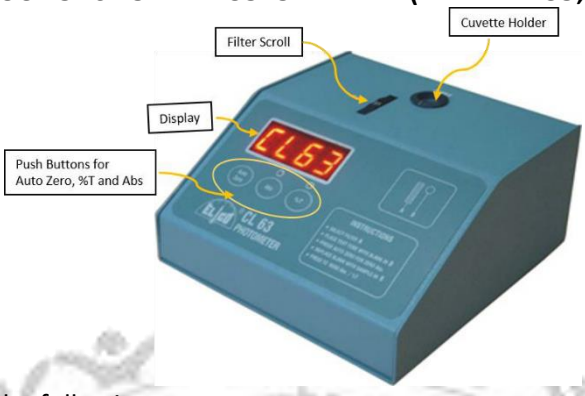
B. Measuring the pH of test solution

(a) Wash the electrode with water, wipe gently with soft tissue and rinse it with the test solution.

(b) Dip the electrode into another fresh aliquot of the test solution, set the instrument to pH or mV mode whichever is required and to Read mode by using standby/Read button.

(c) Read pH (or potential) from display panel. Set the instrument to standby mode. By selecting the mode to mV, the potential may be measured in the same manner as given above.

USAGE INSTRUCTIONS FOR THE COLORIMETER (MAKE: ELICO, SYSTRONICS)



A colorimeter consists of the following:
(a) **A display** which shows absorbance of a sample.
(b) **Filter scroll**: By rotating the scroll (wheel), the desired filter can be selected.
(c) **Cuvette holder (or cell compartment)**: to hold the sample.
(d) **Three push buttons:** (i) Auto Zero for setting absorbance to zero value, (ii) Abs for displaying absorbance, and (iii) %T for displaying the transmittance value.
(e) **Cuvettes or cells:** These are cylindrical in shape and are used to hold the sample. Pathlength is mostly of 1 cm.

Operating instructions:
Switch on the power of Colorimeter at least 15-20 minutes before start of the experiment.

A. Measuring the absorbance of blank:
(a) Take a clean, dry cuvette and fill it with the solvent (most of the time it is water) in which stock solution was prepared.
(b) Wipe off the surface of the cuvette with the help of tissue paper to get rid of solvent and fingerprints.
(c) Insert the cuvette in the sample holder aligning the white mark with the mark on the instrument.
(d) Choose the desired wavelength using Filter knob and set the absorbance to zero using the "Auto Zero" button; this means that the solvent gives 100% transmittance.
(e) Remove the cuvette and pour off the solvent.

B. Measurement of absorbance of test solution
(a) Now rinse and fill the cuvette with solution whose concentration is to be determined (stock solution), dry it from outside using tissue paper and insert it again.
(b) Check that the wavelength is set at the desired value and for which the autozero has been performed.
(c) Note the value of absorbance by pressing the "Abs" button. This will give the absorbance of substance at that particular wavelength.
(d) In case the solution is highly concentrated, absorbance goes out of range and the display does not show any reading, then the sample must be diluted to yield a value within the limits of the instrument.

USAGE INSTRUCTIONS FOR THE VISIBLE SPECTROPHOTOMETER (MAKE: SYSTRONICS MODEL 106)

A visible spectrophotometer (wavelength range of 340 nm – 960 nm) consists of the following:
(a) **A power switch** to set the instrument on/off.
(b) **A display** which shows absorbance/% transmittance of a sample.
(c) **Wavelength knob**: By rotating the knob, the wavelength (in multiples of 5 nm) can be selected.
(d) **Cuvette holders (or cell compartments)**: placed inside the flap, to hold the sample cuvette as well as the cuvette containing the reference liquid (usually the solvent in which the sample is prepared).
(e) **Filter scroll**: placed inside the flap, by rotating the scroll (wheel), the desired filter can be selected.
(f) **Push buttons:** (i) REF switch to perform the reference setting at the desired wavelength for the reference liquid, (ii) Abs/%T toggle switch to select between absorbance or % transmittance, (iii) CAL switch to calibrate the instrument and set either the %T to 100 or Abs to 0, and (iv) a Enter switch to record the Abs/%T value for the sample.
(g) **Cuvettes or cells:** These are glass vials of square cross-section and are used to hold the sample. Pathlength is mostly of 1 cm. Two opposite faces are transparent that allow the incident light to enter and the transmitted light to leave the sample.

Operating instructions:
Switch on the power of the spectrophotometer at least 15-20 minutes before start of the experiment.

A. Measuring the absorbance or % transmittance of blank:
(a) Set the desired wavelength using the wavelength knob, and set the filter to dark using the filter scroll. Set the instrument into the reference mode by pressing the REF switch. Press the Abs/%T toggle switch to select between absorbance or % transmittance.
(b) Take a clean, dry cuvette and fill it with the reference liquid/solvent (most of the time it is water) in which stock solution was prepared.
(b) Wipe off the surface of the cuvette with the help of tissue paper to get rid of the solvent and fingerprints.
(c) Insert the cuvette in the first sample holder aligning the two transparent faces along left and right.
(d) Press the REF switch again either to set the absorbance to 0, or to set the % transmittance 100 [depending on your choice of Abs/%T in step (a)].
(e) Remove the cuvette and set the filter to the appropriate range (in accordance with the selected wavelength) using the filter scroll.

B. Measurement of absorbance or % transmittance of test solution:
(a) Now rinse and fill the cuvette with the test solution whose absorbance or % transmittance has to be recorded, dry it from outside using tissue paper and insert it again.
(b) Press the Enter switch and note down the absorbance or % transmittance value from the display.
(c) Repeat steps (a) and (b) with the rest of the solutions.

USAGE INSTRUCTIONS FOR THE POTENTIOMETER (MAKE: EQUIPTRONICS MODEL EQ-601)

Components of the Potentiometer

(a) **Power switch:** It is located at the back of the instrument. When it is switched on, the display panel in the front glows.

(b) **Control Units of Potentiometer:** All other controls are present on the front panel. A brief description of the various controls meant for potential measurement is tabulated below:

Temperature probe	Connected to the point via a jack and a cable to the metallic probe, dipped in a beaker containing water at room temperature.
Jack point (red)	Point to connect the combined saturated glass calomel electrode.
Jack point (black)	Point to connect the test electrode (usually platinum/silver).
Mode selector switch (IN/OUT)	This is a toggle switch present on the front panel of the instrument. It has the position marked IN and OUT. This is used to set the instrument either at the calibration or read mode. When the toggle switch is in the OUT position, and if the instrument shows a value of 1.019, the instrument is already calibrated. When the toggle switch is in the IN position, it shows the value of the measured EMF in volts.
Adjustment screw	In case the toggle switch is in the OUT position, and the instrument does not show a value of 1.019, this screw is turned clockwise/anticlockwise to achieve this value.

Operating instructions:

(a) Switch on the instrument and give it a warm up time of at least 15 minutes.

(b) Dip the temperature probe into a beaker containing water at room temperature and connect the probe to the jack point at the back panel of the instrument.

(c) Prepare a saturated KCl solution (ensure that there is some undissolved KCl) in a 100 ml beaker and dip the combined glass calomel electrode into the solution.

(d) Connect the glass calomel electrode to the red jack point in the front panel of the instrument.

(e) Ensure that the instrument is calibrated properly, else do the needful as described above.

(f) Pipette out a definite volume of the test solution in another 100 ml beaker and dip the test electrode (usually platinum/silver) in it.

(g) Connect the test electrode to the black jack point in the front panel of the instrument.

(h) Insert the two ends of an appropriate salt-bridge into the two solutions (saturated KCl solution and the test solution).

(i) Homogenise by swirling the test solution carefully (avoid any spillage) and read the EMF value from the display.

USAGE INSTRUCTIONS FOR THE DIGITAL BALANCE (MAKE: METTLER TOLEDO XS-105-DU)

Operating instructions:

(a) Switch on the instrument and give it a warm up time of at least 15 minutes.

(b) Allow the display panel to show 0.0000; if it does not, press the TARE switch.

(c) In case step (b) fails, the instrument is possibly not levelled properly; use a spirit level at different locations of the base of the instrument to check. If the balance is not levelled properly, adjust the screws attached to the pedestals to level the instruments.

(d) Once the instrument shows 0.0000 in a stable manner, you are ready for weighing.

(e) Put a piece of weighing paper, and press TARE to set the zero.

(f) Weigh out the desired amount; while weighing is being carried out, all sorts of mechanical disturbances should be avoided; close the windows on the left and the right-hand sides to avoid such mechanical effects.

(g) Once weighing is over, shut down the balance, switch off the main and cover it with the jacket.