PHYSICAL CHEMISTRY PRACTICAL

Laboratory Manual

SEMESTER 1
B. Sc. Chemistry Hons. Core Course
CEMA-CC-1-P(1)
S. A. Jaipuria College, Kolkata

GENERAL REGULATIONS TO BE FOLLOWED IN THE LABORATORY

1. Never work in the laboratory alone. A minor mishap that may be of little consequence if someone is at hand may help you.
2. Do not throw waste such as compounds, filter papers etc., into the sink. They must be thrown into the separated waste bins.
3. Keep the water and gas taps closed except when these utilities are needed.
4. Never taste any chemical and do not allow chemicals to come in contact with your skin.
5. Wear proper clothes and apron, covered shoes while working in the laboratory.
6. Keep your eye safe from any chemicals, use safety glass if needed.
7. If any chemical sprinkled into your eye, rinse thoroughly with water, seek medical help if necessary.
8. Keep all the doors and windows open while working in the laboratory.
9. Containers in which reaction to be performed should be labeled properly with permanent marker.
10. Working space must be neat and clean and any spillages should be cleaned immediately with proper instructions from the laboratory coordinator.
11. **All graphs need to be plotted in MS-Excel and hard copy to be attached in the laboratory notebook**.

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Experiment 1 _ _

Study of kinetics of decomposition of H_2O_2 (clock reaction)

Theory :

In dilute acid medium (dil. H_2SO_4) H_2O_2 reacts with KI according to

$$H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 + 2H_2O + K_2SO_4 \quad \ldots \quad \ldots \quad (1)$$

Ionically, $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$ ... ... (1a)

t=o a o

t=t (a-x) x

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 :

$$rate = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-] \quad \ldots \quad \ldots \quad (2)$$

where, k is the second order rate constant, [ ] represents molar concentration of the respective species. The unit of k is L mol^{-1} s^{-1} .

The reaction actually occurs in two steps :

i) $H_2O_2 + I^- \xrightarrow{slow} H_2O + IO^-$

ii) $IO^- + 2H^+ + I^- \xrightarrow{fast} H_2O + I_2$

The first step is the rate-determining step.

If the iodide ion concentration, $[I^-]$, is kept constant the reaction becomes kinetically first order in $[H_2O_2]$. This condition is achieved in two ways, (i) by adding sodium thiosulfate solution continuously in small amounts to the reaction mixture, when thiosulfate ($S_2O_3^{2-}$) ions react with the liberated I_2 and regenerate I^- according to

$$I_2 + 2S_2O_3^{2-} = S_4O_6^{2-} + 2I^- \quad \ldots \quad \ldots \quad (3)$$

(ii) using a large excess of I^- ions in the system.

Under these conditions the rate equation (2) is transformed to

$$-d[H_2O_2]/dt = k_1[H_2O_2]$$

where, $k_1 = k[I^-]$

k_1 is the 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=amount of H_2O_2 reacted ≡equivalent of I_2 liberated ≡ equivalent of thiosulfate consumed, one obtains :

$$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right) \qquad \ldots \qquad \ldots \qquad (4)$$

If, V_o= 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 i.e., *a*.

V_t= titre value of the same thiosulfate solution for the iodine liberated by the same volume (10ml) of H_2O_2 present in the reaction mixture (undergoing reaction) at time t; this is equivalent to x.

Substituting for a and (a-x) in the rate equation (4) one obtains the working equation,

$$k_1 = \frac{2.303}{t}\log\frac{V_o}{V_o - V_t} \qquad \ldots \qquad \ldots \qquad (5)$$

$$\therefore \log\frac{V_o}{V_o - V_t} = \frac{k_1}{2.303}.t \qquad \ldots \qquad \ldots \qquad (6)$$

A plot of log $[V_o/V_o-V_t)]$ against t will be a straight line passing through the origin, k_1 may be evaluated from the slope.

Data:

1. Table I: Recording of room temperature:

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

2. Table II: Determination of V_0 (in presence of excess KI) :

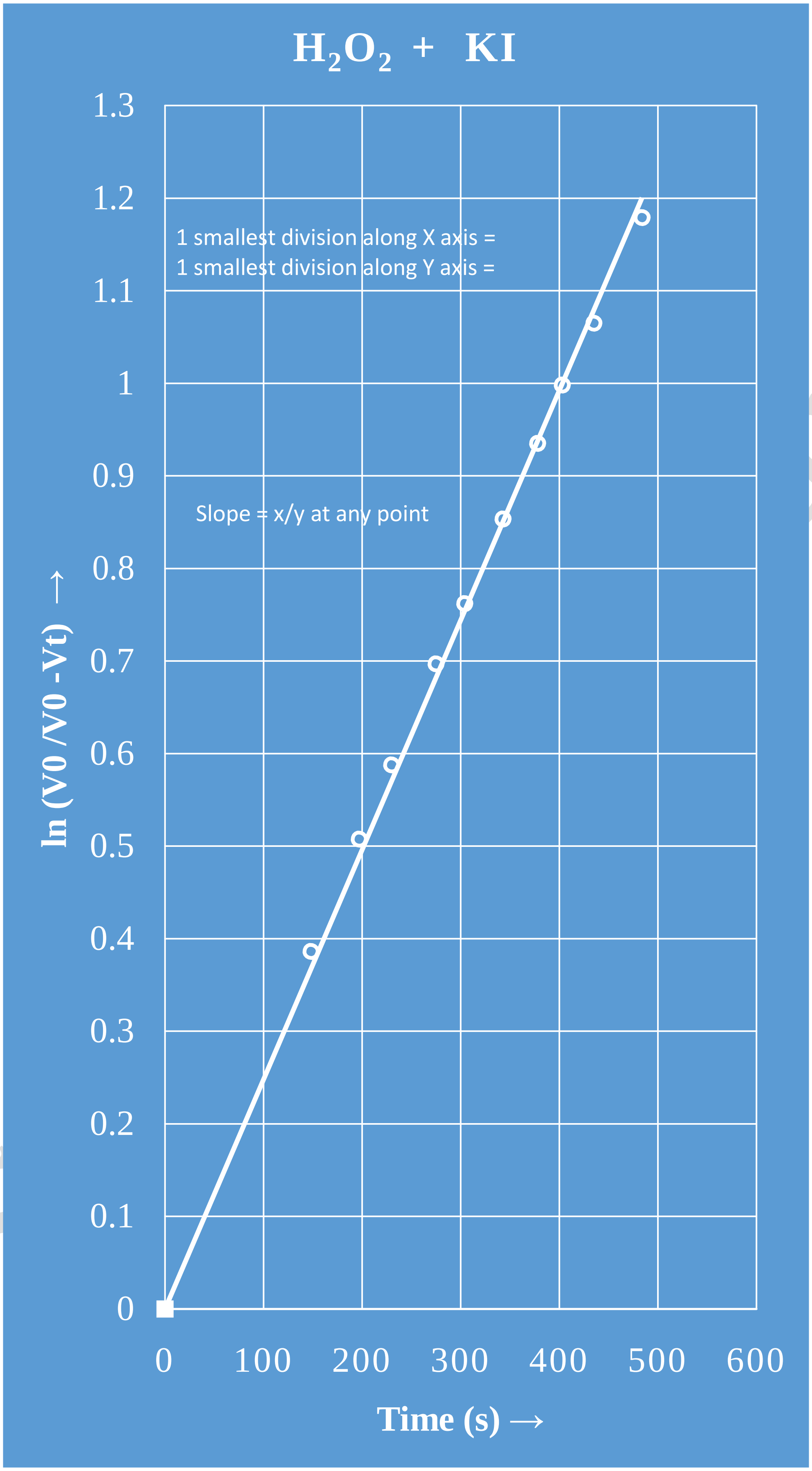
No. of Observations	Volume of '2 Vol' of H_2O_2 (mL)	Initial burette reading	Final burette reading	Volume of thiosulphate soln (mL)	Most probable volume of thiosulphate soln V_0 (mL)

3. Table III: Titre value at different time:

No .of observations	Time (s)	Volume of thiosulphate added in each time (mL)	Total volume of thiosulphate V_t (mL)	V_0 - V_t

4. Table IV: ln(V_0 / V_0 - V_t) vs. Time t (s)

ln(V_0 / V_0 - V_t)											
t (s)											


H_2O_2 + KI
1 smallest division along X axis =
1 smallest division along Y axis =
Slope = x/y at any point
ln (V0 /V0 -Vt) →
Time (s) →
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
0
100
200
300
400
500
600

Experiment 2

Study of kinetics of acid catalyzed hydrolysis of methyl acetate

Theory :

Rate of 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 Products ... ... (1)

for which the rate,

$$\frac{-dC_A}{dt} = kC_{A'} \quad \ldots \quad \ldots \quad (2)$$

where, k, is the rate constant (unit : time^{-1}) and C_A is the molar concentration of A at time t. Integration of the rate equation with proper limits at t=0, $C_A=C_o$ and at t=t, $C_A=C_t$, converting the logarithmic term to base 10 (i.e., $\log_{10}$) one obtains,

$$k = \frac{2.303}{t}\log_{10}\frac{C_o}{Ct} \quad \ldots \quad \ldots \quad (3)$$

Hydrolysis of an ester (e.g. methyl acetate) although appearing to be bimolecular is kinetically a first order reaction with respect to the ester, since, water is present in large excess. The rate of the reaction also depends on the concentration of H$^+$ ion but H$^+$ being a catalyst is not consumed in the reaction and consequently its concentration remains constant in a given set.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH \quad \ldots \quad \ldots \quad (4)$$

The reaction is slow but is efficiently catalyzed by strong acids (say HCl; H$^+$ is the active ion). When a known amount of an ester (methyl acetate) is allowed to hydrolyse in 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 an alkali solution using phenolphthalein as indicator. The volume of alkali required for a known volume of 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_o, V_1 and V_∞ be the volumes of the alkali required for the same volume of the aliquots–at the beginning, (t=0), at time t and at the end of the reaction (infinite time, t=∞), then,

$(V_\infty - V_o) \propto C_o$, initial concentration of the ester ... ... (5)

$(V_t - V_o) \propto$ concentration of ester consumed = concentration of weak acid formed

$\therefore$ Concentration of ester left $\propto [(V_\infty - V_o) - (V_t - V_o)] \propto (V_\infty - V_t) \propto C$

Substituting in eqn (3)

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

$$\therefore \log_{10}\left(\frac{V_\infty - V_o}{V_\infty - V_t}\right) = \left(\frac{k}{2.303}\right).t \qquad \ldots \qquad \ldots \qquad (6)$$

Consequently since it is not possible to determine V_o for the reaction, the first volume of NaOH, i.e V_1 will replace V_o, consequently t will be replaced by Δt, where, $\Delta t = t_n – t_1$, n=2, 3, 4,...etc.

Thus, measuring V_1, V_t and $V_\propto$and plotting $\log_{10}$ [$V_\propto – V_1$) / ($V_\propto – V_t$)] against Δt, it is possible to determine k from the slope of the resulting straight line passing through the origin.

$$k=2.303\times\text{slope} \qquad \ldots \qquad \ldots \qquad (7)$$

Data:

1. Table I: Recording of room temperature:

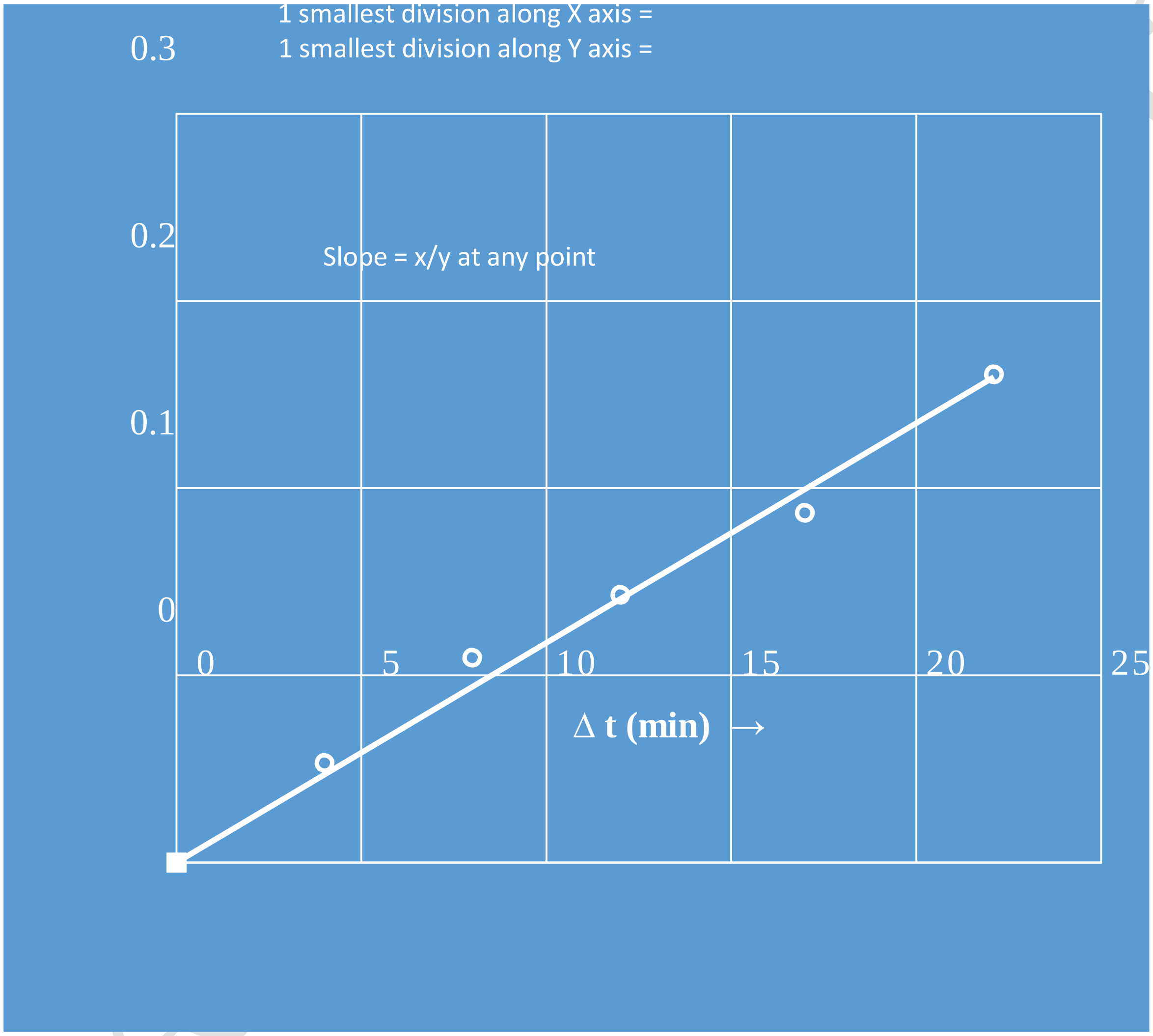
Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

3. Table II: Ester Hydrolysis with 1(N) HCl

No. of observations	Time t_n (s)	Volume of Ester (mL)	Volume of NaOH (mL)	V_∞ (mL)	V_∞ - V_1 (mL)	V_∞ - V_t (mL)

4. Table of ln $(V_\infty - V_1/ V_\infty - V_t)$ vs. Δt

ln $(V_\infty - V_1/ V_\infty - V_t)$				
$\Delta t = t_n - t_1$				



Experiment 3

Study of viscosity of unknown liquid With respect to water

Theory :

Viscosity is the property which opposes the relative motion of adjacent layers of a liquid and can be regarded as a type of internal friction. *Newton's law* of viscous force is applicable when a liquid flows slowly and executes streamline motion. The law states that, the force (f) required to maintain a velocity difference of dV_x (in the x-direction) between two parallel layers of area, A, separated by a distance of dz in the z-direction) is given by :

$$f = \eta A \frac{dV_x}{dz} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

Where (η) is the *viscosity coefficient* of the liquid which is defined as the force per unit area required to maintain a unit velocity gradient (in the x-direction). The (c.g.s.) unit of η is *poise* and 1 poise = 1. dyne.sec.cm^{-2}. The magnitude η of depends on temperature. η decreases by about 2% per degree Celsius rise in temperature.

The viscosity coefficient (η) may be determined experimentally using an Ostwald viscometer which utilizes the Poiseuille's equation,

$$\eta = \frac{\pi r^4 t P}{8 V l} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (2)$$

This equation is valid for an incompressible fluid (i.e. a liquid) flowing very slowly (streamline motion) through a narrow tube of radius, r, and length, l, under an average pressure of P, when there is a flow of V volume of the liquid in time t.

If t_1 and t_2 be the times of fall of a definite volume of two liquids (1 and 2) through the same Ostwald viscometer and η_1 and η_2 be their viscosity coefficients, and P_1 and P_2 respectively be the average pressures, then one may obtain from eqn. (2).

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (3)$$

The pressure P, driving the liquid through the capillary at any instant, is equal to hdg, where h is the difference in height between the levels of the liquid in the two limbs, d is the density of the liquid and, g is the acceleration due to gravity. During the experiment, P decreases with time as h decreases. The initial height difference (h_1) and the final height difference (h_2), ($h_1 > h_2$), are same for both the liquids, since the same volume of the two liquids are allowed to pass through the capillary tube. Thus, the average pressures P_1 and P_2 may be expressed as :

$$P_1 = [(h_1 + h_2) / 2]\, d_1 g$$

and

$$P_2 = [(h_1 + h_2) / 2]\, d_2 g$$

Thus,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \qquad \ldots \qquad (4)$$

In the Ostwald viscometer a definite volume of a reference liquid (water) is introduced in the wider arm of the instrument, the liquid is sucked into the narrower arm and the time required for a fixed volume of the liquid to flow through the capillary under the action of gravity is noted. The procedure is repeated for the experimental liquid (L). (Picture given below)

When water (w) is used as the reference liquid, the expression (4) is transformed to (5).

$$\frac{\eta_L}{\eta_w} = \left(\frac{d_L}{d_w}\right)\left(\frac{t_L}{t_w}\right) = S_L \frac{t_L}{t_w} \quad \dots \quad \dots \quad \dots \qquad (5)$$

$$\eta_L = S_L \left(\frac{t_L}{t_w}\right) \eta_w \quad \dots. \quad \dots. \quad \dots\dots \quad \dots\dots \quad \dots\dots. \quad \dots\dots \qquad (6)$$

where, η_W, η_L, d_L, t_W, t_L, have their usual meaning and S_L is the specific gravity of the liquid. Thus, if the viscosity coefficient (η_W) of water is known, the viscosity coefficient (η_L) of the liquid can be determined by determining the specific gravity (S_L) of the liquid and measuring the times of flow t_W and t_L of a definite volume of water and the liquid respectively. Additives like ethanol, glycerol or cane sugar increase the viscosity coefficient.

Data:

1. Table I: Recording of room temperature:

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

2. Table III: Determination of required time of flow using viscometer:

Liquid	Time taken by liquid (s)	Mean time taken (s)
Water		
Sample		
½ diluted Sample		

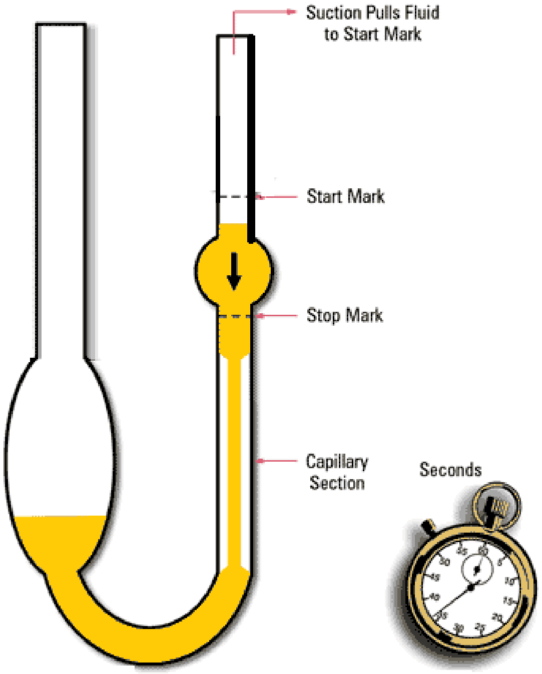
3. Table II : Determination of specific gravity of the liquid:

Liquid	Wt. of the empty bottle (W_1) g	Wt. of the bottle with water (W_2) g	Wt. of the bottle filled with the liquid (W_3) g	Specific gravity of the liquid $S_L = (W_3-W_1)/(W_2-W_1)$
Sample				
½ diluted sample				

4. Calculations:

Viscosity coefficient $\eta_L = (t_L/t_W).\ S_L.\ \eta_W$
$= f.\ S_L.\ \eta_W$

[p. n. $\eta_L > \eta_W$]



Experiment 4

Study of variation of viscosity with the concentration of the solution

Theory:

In the Ostwald viscometer a definite volume of a reference liquid (water) is introduced in the wider arm of the instrument, the liquid is sucked into the narrower arm and the time required for a fixed volume of the liquid to flow through the capillary under the action of gravity is noted. The procedure is repeated for the experimental liquid (L). (Picture given below)

When water (w) is used as the reference liquid, the expression (4) is transformed to (5).

$$\frac{\eta_L}{\eta_w} = \left(\frac{d_L}{d_w}\right)\left(\frac{t_L}{t_w}\right) = S_L \frac{t_L}{t_w} \quad \ldots \quad \ldots \quad \ldots \qquad (5)$$

$$\eta_L = S_L \left(\frac{t_L}{t_w}\right)\eta_w \quad \ldots. \quad \ldots. \quad \ldots\ldots \quad \ldots\ldots \quad \ldots\ldots. \quad \ldots\ldots \qquad (6)$$

where, 'η_W’η_L’ d_L’ t_W’ t_L’ have their usual meaning and S_L is the specific gravity of the liquid. Thus, if the viscosity coefficient (η_W) of water is known, the viscosity coefficient (η_L) of the liquid can be determined by determining the specific gravity (S_L) of the liquid and measuring the times of flow t_W and t_L of a definite volume of water and the liquid respectively. Additives like ethanol, glycerol or cane sugar increase the viscosity coefficient.

To determine the concentration (%) of a given solution of glycerol (or sucrose), a number of solutions different concentrations are prepared and viscosity coefficients of all the solutions are measured Ostwald’s Viscometer. η of the given unknown solution is also measured. Now a plot of η vs. C (in %) is drawn, which will be a straight line with positive slope. From the graph, the percentage concentration of the given unknown solution is estimated against the corresponding value.

Data:

1. Table I: Recording of room temperature:

Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

2. Table II: Preparation of Sucrose solution with different concentrations:

Weigh out exactly 30g solid sucrose in a 250 ml volumetric flask, dissolve it in water and make up the volume up to the mark. Then prepare other concentrations in 100ml beakers using burette from this stock solution.

Volume of stock sucrose (12%) ml	Volume of water (ml)	Final concentration of the soln. (%)
37.5	12.5	9.0
30	20	7.2
25	25	6.0
12.5	37.5	3.0

3. Table III: Determination of specific gravity of the solutions:

Conc. of the solutions (%)	Wt. of the empty bottle (W_1) g	Wt. of the bottle with water(W_2) g	Wt. of the bottle filled with the solutions (W_n) g	Specific gravity of the solutions $S_L = (W_n-W_1)/(W_2-W_1)$
Water (0.0)				
3.0				
6.0				
7.2				
9.0				
12.0				
Unknown				

4. Table IV: Determination of required time of flow using viscometer:

η_w at ___________ ^{o}C = ______________ poise

Solutions (%)	Time taken by liquid (sec)		Mean time taken (sec) t_L	Sp. gravity of the solutions S_L	$\eta_L = \eta_w S_L (t_{L/}\ t_w)$
Water (0.0)					
3.0					
6.0					
7.2					
9.0					
12.0					

5. Table for η vs. concentration (%):

%	0.0	3	6	7.2	9	12	
η(centipoise)							

Experiment 5

Determination of solubility and solubility product of a sparingly soluble salt in water and in various electrolytic media by titrimetric method.

Theory :

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 undissolved solute. If S_o be the solubility, then the concentration of the saturated solution is 10 S_o/M molal where M is the molar mass of the solute. Saturated solutions of sparingly soluble salts are sufficiently dilute; as such the concentrations in molarity are very close to molality. For such solutions molar concentrations may conveniently be used as the measure of their solubility.

Solubility product of a sparingly soluble electrolyte is the product of the activities of the ions (raised to proper power), in a saturated solution at a particular temperature. Solubility equilibrium of a 1 : 1 sparingly soluble salt, A^+B^-, in aqueous medium may be represented according to :

$$A^+B^- \text{ (solid)} \qquad\qquad A^+ \text{ (aq)} + B^- \text{ (aq)} \qquad \ldots \qquad (1)$$

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

$$K_a = a_{A^+} \times a_{B^-} \qquad \ldots \qquad (1a)$$

$$K_c = [A^+] \times [B^-] \qquad \ldots \qquad (1b)$$

Where *a* represents activity and [ ] represents molar concentration of the aquated ions.

Since, activity (a) = Concentration × activity coefficient, i.e.,

$$a_{A^+} = [A^+].f_{A^+} \text{and } a_{B^-} = [B^-].f_{B-}$$

$$\therefore K_a = K_c.(f_{A^+}.f_{B^-}) = K_c.(f_\pm)^2 \qquad \ldots \qquad (1c)$$

here, $(f_\pm)$ is the mean ionic activity coefficient of the electrolyte.

As the saturated solution of a sparingly soluble salt is very dilute, the activities of the ions become numerically equal to their molar concentrations since the mean activity coefficient (f_+) tends to unity, therefore,

$$K_a = K_c = S_o \times S_o = S_o^2 \qquad \ldots \qquad \ldots \qquad (2)$$

where, S_o = solubility of the salt (A^+B^-) in mole per litre in water.

Potassium hydrogen tartrate (KHTa) is a sparingly soluble salt. In aqueous solution it ionises according to,

$$\mathrm{KHTa}(s) \rightleftharpoons \mathrm{K^+ (aq) + HTa^- (aq)} \quad \ldots \quad \ldots \quad (3)$$

If the concentration of HTa^- ion in the saturated solution of KHTa in water at room temperature is S mole/litre, then the concentration solubility product, K_c, may be obtained from the relation:

$$K_c = S^2 \quad \ldots \quad \ldots \quad (4)$$

Solubility (S´) of the salt (KHTa) in a solution containing a common ion (e.g. KCl), is lower than that in pure water. Since the solubility product (K_a) is a constant,

$$Ka = K_c = (S´ + C)\, S´ \quad \ldots \quad \ldots \quad (5)$$

where, C, is the concentration of the electrolyte (KCl). In the presence of an electrolyte having no ions in common (e.g. $NaNO_3$), the ionic strength of the medium increases, and the mean ionic activity coefficient decreases (a consequence of *Debye-Huckel limiting law)* and there is a consequent increase of solubility (S) of the sparingly soluble salt (cf. eq. 1c). As a result, K_c increases since K_a at a particular temperature remains unchanged.

Data:

1. Table I: Recording of room temperature:

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

2. Table II: Preparation of standard oxalic acid solution:

Initial wt. (W_1) g	Final wt. (W_2) g	Wt. transferred (W_2-W_1) g	Strength of solution

3. Table IV: Standardization of NaOH solution:

No. of Observations	Volume of oxalic acid taken (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)

Strength of NaOH S_0 =

4. Table V: Titration of KCl +KHTa with NaOH:

No. of Observations	Volume of KCl+KHTa(mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)

Strength of NaOH S_0' (KCl +KHTa) =

5. Table VI: Titration of water + KHTa with NaOH:

No. of Observations	Volume of KCl+KHTa (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)

Strength of NaOH S_0 (water + KHTa) =

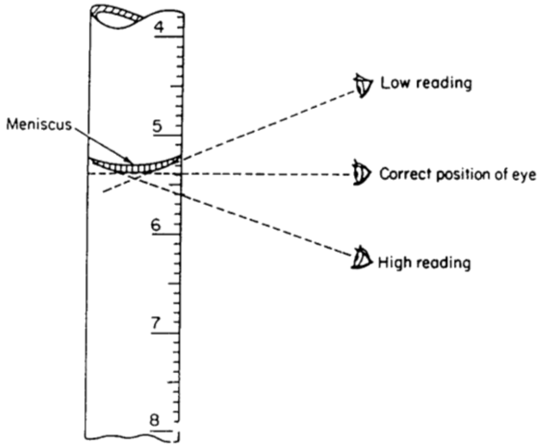
Calculations:

Solubility of KHTa in water (g mol/L and g/L) =

(Solubility range 3.8-4.4 x 10^{-2} g mol/L in water)

Solubility of KHTa in KCl solution (g mol/L and g/L) =

(Solubility range 1.55-2.15 x 10^{-2} g mol/L in KCl)



Position of eyes for accurate Burette reading

Therefore the solution contains one common ion with the salt.

[Note: If solubility of KHTa is 4.7-5.2 x 10^{-2} g mol/L in solution, then the solution contains no ion common with the salt]