Experiment No 1 : To study the kinetics of inversion of cane sugar using a polarimeter.

Theory :

Inversion of cane sugar (sucrose) takes place due to its hydrolysis in the presence of H^+ ions as catalyst in aqueous medium to produce glucose and fructose in equimolar proportion.

$$C_{12}H_{22}O_{11} \quad + \quad H_2O \longrightarrow C_6H_{12}O_6 \quad + \quad C_6H_{12}O_6 \qquad \ldots \ldots (1)$$

	(sucrose)	(water)	(glucose)	(fructose)
t=0	a		0	0
t=t	(a-x)		x	x
t= ∞	0		a	a

Since sucrose is *dextro-rotatory* (specific rotation +66.5) whereas the hydrolysed mixture consisting of equimolar quantities of glucose and fructose is *laevo-rotatory* (specific rotations + 52.7 and -92.0 respectively at 25°C), an inversion in the sign of optical rotation of the solution occurs due to this reaction which signifies the term *inversion*.

The rate of the reaction (1) depends upon the concentrations of sucrose, water and hydrogen ions. Water being present in large excess, its concentration remains virtually unchanged. Concentration of the H^+ ion also remains unchanged since it is not used up in the reaction. So, the rate of the reaction (1) is proportional to concentration of sucrose only. Thus the 'inversion' reaction (1) becomes kinetically of the *first order*.

The rate law of the reaction may be expressed according to (2) :

$$\text{rate} = -\frac{d}{dt}[\text{sucrose}] = \frac{d}{dt}[\text{glucose}] = \frac{d}{dt}[\text{fructose}] = k[\text{sucrose}] \qquad \ldots \quad \ldots \quad (2)$$

where [ ] represents concentration in mol L^{-1}, k is the first order rate constant.

If *a* is the initial concentration of sucrose at time, t=0 and x is the concentration of sucrose decomposed during time t=t, then (a-x) is the concentration of sucrose remaining at time t=t. The rate equation (2) may be expressed as :

$$-\frac{d}{dt}(a-x) = k(a-x) \qquad \ldots \quad \ldots \quad (3a) \quad \text{or,}$$

$$\frac{dx}{dt} = k(a-x) \qquad \ldots \quad \ldots \quad (3b)$$

On integrating one obtain:

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

If the quantities , $x_1, x_2, \ldots x_n$ etc., or $(a-x_1)$, $(a-x_2)$,.....$(a-x_n)$ etc., are determined at different intervals of time respectively, then on rearranging equation (4) one obtains

$$\log_{10}\left(\frac{a-x_1}{a-x_n}\right)=\frac{k}{2.303}(t_n-t_1) \qquad \ldots \qquad \ldots \qquad (5)$$

where, t_n and x_n represent the corresponding data of n-th recording, $(n>1)$. This formulation eliminates the need for accurate determination of the initial concentration *a*. The optical rotation (θ) is proportional to concentration of the optically active substance. If θ_o, and θ_∞ are the corrected angles of rotation at the beginning ($t=0$) and at the end ($t=\infty$) of the reaction, and θ_1 and θ_n be the values at times t_1 and t_n, then ($\theta_o-\theta_\infty$) will be proportional to the initial concentration *a*, ($\theta_1-\theta_\infty$) will be proportional to ($a-x_1$) and ($\theta_n-\theta_\infty$) will be proportional to ($a-x_n$) respectively. The relation (5) is thus transformed to (5a) :

$$k=\frac{2.303}{t_n-t_1}\log_{10}\left(\frac{\theta_1-\theta_\infty}{\theta_n-\theta_\infty}\right) \qquad \ldots \qquad \ldots \qquad (5a)$$

Thus, k can be determined from the slope of straight line obtained by plotting logarithmic terms of eqn. 5(a) against time interval (t_n-t_1).

Since the strong acid (the catalyst) is completely dissociated at the concentration employed, the rate constants (k_I and k_{II}) of the reaction with two sets of concentrations of the strong acid are directly proportional to their concentrations $[\text{acid}]_I$ and $[\text{acid}]_{II}$.

$$\frac{k_I}{k_{II}}=\frac{[acid]_I}{[acid]_{II}} \qquad \ldots \qquad \ldots \qquad (6)$$

It is assumed that the rate of reaction in pure water (only) is negligible.

Eq (6) indicates that the reaction is first order with respect to the catalyst (H^+ ion), which implies that H^+ ion is a homogeneous catalyst for this reaction.

Data:

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Preparation of solution of Sucrose:

Solution	Wt. of Sucrose (g)	Vol. of water (ml)	% concentration w/V
Solution A	60	200	30 %
Solution B	Diluted from solution A: (X * 30%= 100*21%) X= 70 ml of solution A + 30 ml of water		21%

Table III: Recording of angle of rotation for solvent water for instrumental error:

Least count (lc) =

Main scale reading (m)	Vernier scale reading (v)	Total reading = m + v*lc

Table IV: Recording of angles of rotation θ for two sets with time:

	No. of obs	**Time (sec)**	**Optical rotation (θ)in degrees**
Set I **(with solution A)**			
Set II **(with solution B)**			

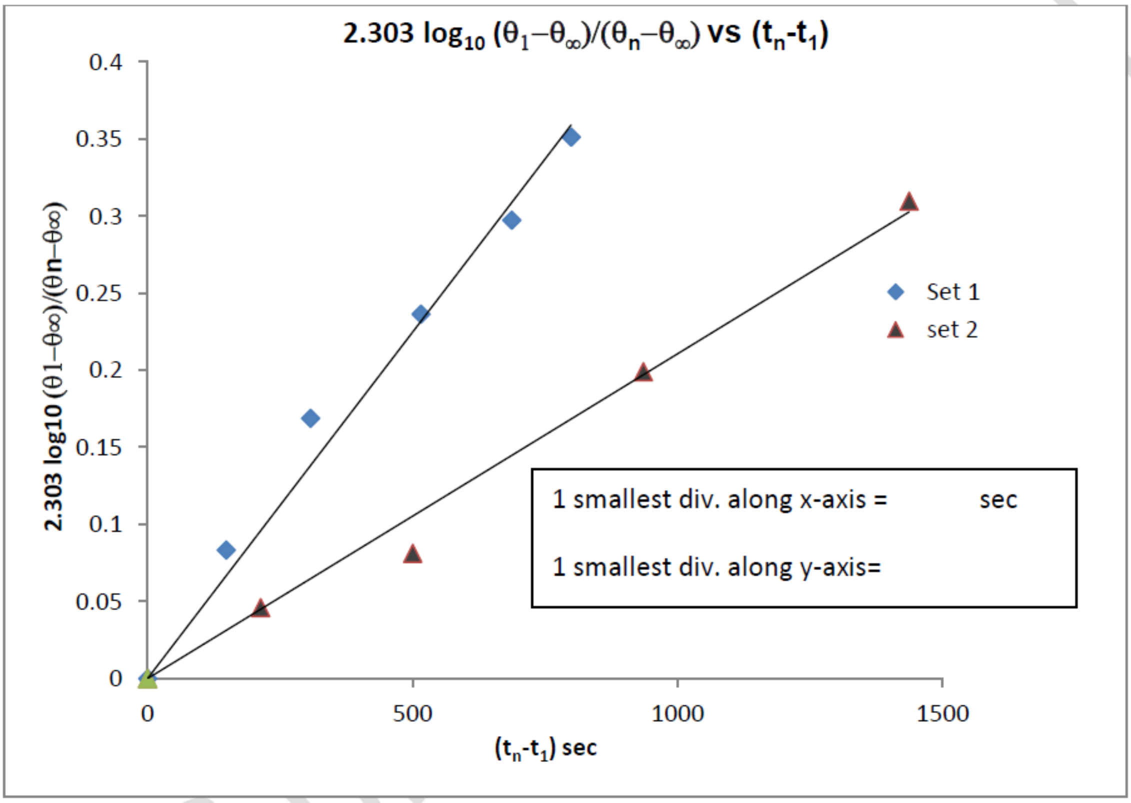
Table V: Recording of θ_∞ for both sets:

	Set I	Set II
θ_∞ in degrees		

Calculations: For plotting of the graphs

Table VI: Plotting of graph 2.303 $\log_{10} (\theta_1-\theta_\infty)/(\theta_n-\theta_\infty)$ vs. (t_n-t_1) sec.

	Value of n	n=1	n=2	n=3	n=4	n=5	n=6
Set I	2.303 $\log_{10} (\theta_1-\theta_\infty)/(\theta_n-\theta_\infty)$						
	(t_n-t_1)						
Set II	2.303 $\log_{10} (\theta_1-\theta_\infty)/(\theta_n-\theta_\infty)$						
	(t_n-t_1)						



Calculations: (from the graph)

Slope for Set-I:

Slope for Set-II:

Ratio of the slopes:

Experiment No 2 : To study the phase diagram of a binary system (phenol-water) and the effect of impurities (eg. NaCl)

Theory :

A diagram representing the conditions of equilibrium among different forms or phases of a substance or of a mixture of substances is called a phase diagram. When the position of such an equilibrium is influenced only by such variables as temperature, pressure and concentration, but not by such factors as gravity, surface tension, electrical and magnetic forces, the number of degrees of freedom (F) of the system may be related to the number of components (C) and the number of phases (P) according to the

phase rule equation. **F=C–P+2**

In a binary mixture of two partially miscible liquids e.g., phenol and water, two phases are formed. When water is gradually added to phenol, water passes into solution until a saturated solution of water in phenol is obtained. A new phase of different density, consisting of a saturated solution of phenol in water appears on addition of further quantities of water. Increase in the concentration of water increases the volume of the second phase (i.e., phenol in water) and decreases the volume of the first phase (i.e., water in phenol), but the relative concentrations of the components in either phase remain constant. Such mutually saturated liquid pairs in contact with the each other constitutes a *univariant system,* the only variable being the temperature, the pressure being kept constant .Rise of temperature brings about a change in the mutual solubilities of the two liquids. The solubility curve of phenol water system (Fig. 1) shows that the mutual solubilities increase with increase of temperature. The two phases have a unique composition called *consolute composition* at a certain temperature (tc) called *critical solution temperature (CST), or, consolute temperature (CT)*. For phenol water system tc=65.9°C is the *upper critical solution temperature (UCST)* and the consolute composition is, water 66% and phenol 34%. Above this temperature the two liquids are completely miscible. The liquid pair indicated by any point (x) in between the two solubility curves will separate into two phases indicated by two points A and A´, while any liquid pair represented by any point outside the curve will form a single phase. Lines (such as A A´) joining the two mutual solubilities at any given temperature are called *tie-lines* and the two solutions represented by the compositions A and A´ are called *conjugate solutions.* As pressure is fixed throughout the experiment, F=C–P+1=2-1+1=2. That is such a system will be bivariant. So only two degrees of freedom -temperature and composition, should be specified in order to define the system completely. In region under the solubility curve there are two phases, i.e., P=2, C=2 (as before), hence, F=C-P+1=2-2+1=1. That is, such systems will be univariant, the temperature alone will define the system completely. Therefore, the two phases at any given temperature will have definite compositions, irrespective of their amounts.

At any point on the solubility curves, say at A or A´, C=2 and P=2, one of two conjugate solutions has a mere existence. Hence, F= C- P +1 = 2- 2 + 1 = 1, i.e., solubility has a definite value at a particular temperature.

At the point x′ on this curve, the two conjugate solution have identical composition, C=2−1=1, P=2, hence, F= C-P + 1 = 1- 2 +1 = 0, So, the system represented by this point x′ is *invariant,* since temperature (tc) and composition are automatically fixed.

When a third substance, such as, NaCl is added to a binary mixture of two partially miscible liquids (e.g., phenol-water) the mutual solubility of the liquids will depend upon the chemical nature and quantity of the third substance. Mutual solubilities generally decrease when the third substance is soluble only in one of the two liquids, and consequently consolute temperature rises. When the third substance dissolves in both the liquids consolute temperature is generally lowered.

If we calculate mean values of the compositions of the two conjugate solutions at several temperatures, and plot these points against corresponding temperatures, a straight line will always be obtained, which passes through the critical composition at the critical temperature. This ‘‘law of rectilinear diameter’’ as applied to partially miscible liquid pairs is obviously an extension of the corresponding law of Cailletet and Mathias on critical phenomena in the liquid-gas equilibrium.

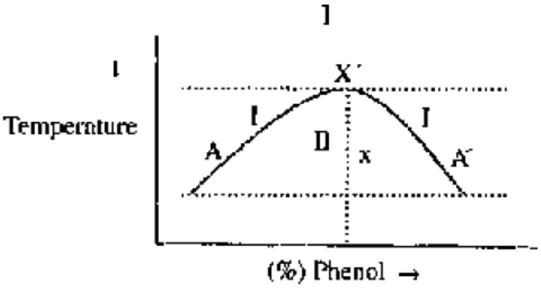


Fig. 1. Solubility curve of phenol-water system

Data:

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Weighing of phenol:

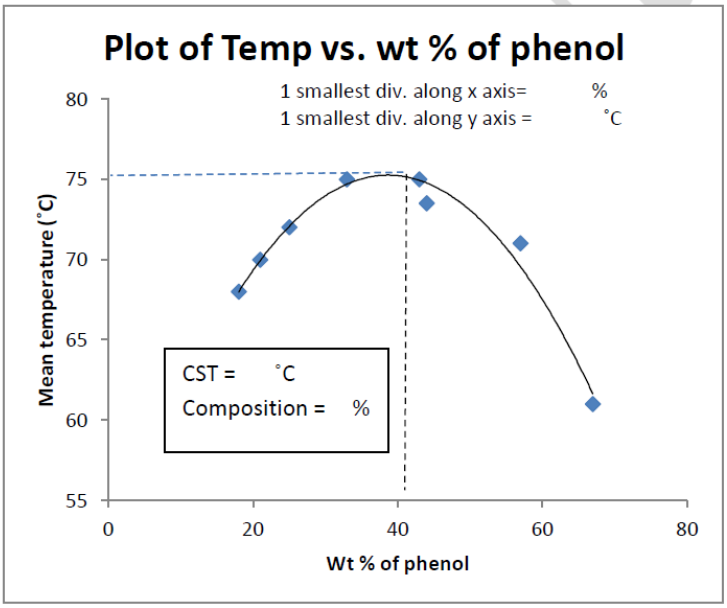
Initial wt. (g)	Final wt. (g)	Weight taken (W_1) g

Table III: Recording of miscibility temperatures around CST for volumes of PD added:

No. of Obs.	Temperature of Disappearance (T_1 °C)	Temperature of Reappearance (T_2 °C)	Mean Temp T= $(T_1+T_2)/2$ (°C)	Vol. of PD (ml)	Wt. of PD added (W_2) g	Wt % of Phenol W = $\frac{W_1 * 100}{(W_1+W_2)}$

Table IV: Plot of Temperature vs wt % of phenol:

Mean Temp. T (°C)										
Wt % of Phenol (W %)										



Calculation:

From Graph,

UCST = ˚C

% Wt of Phenol =

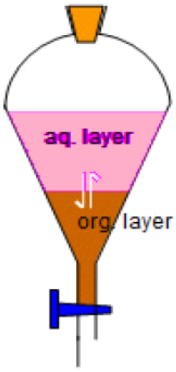
Experiment No 4 : Determination of partition coefficient of Iodine or Acetic acid between water and an immiscible organic solvent.

Theory :

According to *Nernst distribution law,* if to a system consisting of two immiscible or slightly miscible liquids is added a third substance, which is soluble in both the liquids, the substance distributes itself between the two liquids in such a manner that the ratio of its molar concentrations (precisely, the activities) in the two liquids remains constant at a particular temperature.

The following equilibrium is established when iodine (I_2) is added to water in presence of an immiscible organic solvent :

$$I_2 \text{ (water)} \rightleftharpoons I_2 \text{ (organic solvent)} \quad \ldots \quad (1)$$



The solute iodine distributes between the organic (carbon tetrachloride) solvent and water at equilibrium.

$$I_{2(aq)} \rightleftharpoons I_{2(organic)}$$

Thus if and be the activities of the solute (I_2) in the two liquids, water (w) and organic solvent (o) at equilibrium, then,

$$K_d = \frac{(a_{I_2})_o}{(a_{I_2})_w} = \text{constant} \quad \ldots \quad \ldots \quad (2)$$

The constant, K_d is the *distribution coefficient,* or, the *partition coefficient* of the solute (I_2) between the two liquids, organic solvent and water. This expression holds good so long as the solute retains the same state of aggregation in the two solvents, i.e., there is neither association nor dissociation of the solute in the two solvents and there occurs no chemical reaction between the solute and the solvents or even between the solvents.

If both the phases are dilute solutions, then, the activity coefficients are very close to unity and molar concentration of the solute (I_2) in the two phases, $[I_2]_W$ and $[I_2]_O$ approach their activities and respectively, and distribution coefficient, $K_{d'}$ is then given by,

$$K_d = \frac{[I_2]_o}{[I_2]_w} \quad \ldots \quad \ldots \quad (3)$$

Thus, by determining the concentrations of I_2 in the two liquid layers by titrating with a reducing agent, eg., sodium thiosulfate using starch indicator it is possible to determine the value of K_d at room temperature.

Thiosulfate ($S_2O_3^{2-}$) is oxidized by I_2 to tetrathionate ($S_4O_6^{2-}$) according to,

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^{-} + S_4O_6^{2-} \quad \ldots \quad \ldots \quad (4)$$

If V_1 ml of the aqueous layer of iodine requires for titration T_1 ml of S (N) thiosulfate solution, and V_2 ml of organic layer of iodine requires T_2 ml of x S(N) thiosulfate solution (x >1), then the partition coefficient, K_d, will be :

$$K_d = \frac{T_2.x.S/V_2}{T_1.S/V_1} = x\left(\frac{T_2}{T_1}\right)\left(\frac{V_1}{V_2}\right) \quad \ldots \quad \ldots \quad (5)$$

Data:

1. Table I: Recording of room temperature:

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

2. Table II: Titration of Aqueous Layer:

Set No.	No. of Observations	Volume of aqueous layer (mL)	Initial burette reading	Final burette reading	Volume of thiosulphate (mL)	Most probable volume of thiosulphate (mL)

3. Table III: Titration of Organic layer:

Set No.	No. of Observations	Volume of aqueous layer (mL)	Initial burette reading	Final burette reading	Volume of thiosulphate (mL)	Most probable volume of thiosulphate (mL)

Calculations:

Experiment 5/6: Determination of pK values of weak monobasic, dibasic and polybasic acid by pH–metric method.

Theory :

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

$$\text{Ag}\left|\text{AgCl(s)}\right|\text{0.1(M)HCl}\left|\text{Glass}\right|\begin{array}{c}\text{Solution}\\ \text{of}\\ \text{unknown}\\ \text{pH}\end{array}\left|\begin{array}{c}\text{Saturated}\\ \text{Calomel electrode}\end{array}\right.$$

The right hand electrode is the saturated calomel electrode (SCE) and the left hand electrode is the glass electrode which is actually an ion selective membrane electrode, reversible with respect to H^+ ion. The glass electrode is the most widely used hydrogen ion responsive electrode and its use depends on the fact that when a glass membrane is immersed in a solution, a potential is developed which is a linear function of the hydrogen ion concentration of the solution. The internal HCl solution is maintained at constant concentrations, the potential of the silver-silver chloride electrode inserted into it will be constant, and so too will the potential between HCl solution and the inner surface of the glass bulb. Hence the only potential which can vary is the potential between the outer surface of the glass bulb and the test solution in which it is immersed, so the overall potential of the electrode is governed by the hydrogen ion concentration of the test solution. Glass electrodes are also available as combination electrode which contain the indicator electrode and a reference electrode combined in a single unit. The potential (E_g) of the glass electrode at 25°C may be expressed as,

$$E_g = E^\circ_g + 0.059 \log a_{H+}$$

$$= E^\circ_g - 0.059\ \text{pH} \qquad \ldots\ \ldots \qquad (1)$$

For actual pH measurement, the glass electrode is standardised in buffer solutions of known pH values.

Ionisation of a weak monobasic (HA) in aqueous solution may be represented as,

$$HA \rightleftharpoons H^+ + A^- \qquad \ldots\ \ldots \qquad (2)$$

of which the ionisation constant (K_a) is given by the activity quotient of the ionisation equilibrium (2),

$$K_a = \frac{a_{H^+} . a_{A^-}}{a_{HA}} \qquad \ldots\ \ldots \qquad (3)$$

where, *a* represents activity of the respective species which is related to the molar concentration, (c) according to a = c.f., where f = activity coefficient. In dilute aqueous solutions of weak acids, ionic strength is very low, so the activity coefficients approach unity, hence the concentrations approach activities. Consequently the ionisation constant (K_a) may be expressed as

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots\ \ldots \qquad (4)$$

When a strong base NaOH is added to a weak acid acetic acid in an amount less than the stoichiometric requirement a buffer solution is form the pH of which is given by the Henderson's Equation.

$$pH = pK_a + \log_{10}\frac{[Salt]}{Acid]} \qquad \ldots\ \ldots \qquad (5)$$

If the amount of base added is just half-equivalent of the acid present, then [salt]=[acid]

and $pK_a = (pH)_{1/2}$ … … (6)

where, represents the pH of the solution at the half neutralization point. The pK_a value of a weak acid is most conveniently determined pH metrically by titrating the weak acid with a strong base. 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 the neutralization point may be read out from the pH-metric titration curve.

For dibasic acids like oxalic or succinic acid (H_2A), the ionization equilibria may be expressed as,

$$H_2A \rightleftharpoons HA^- + H^+ \qquad (K_1)$$

$$HA^- \rightleftharpoons A^{2-} + H^+ \qquad (K_2)$$

where, K_1 and K_2 are dissociation constants for the first and second step of dissociation respectively.

For oxalic/succinic acid beyond the half-equivalence point the system is a buffer consisting

of HA^- and A^{2-}. The pH of this buffer solution is given by :

$pH = pK_2 + \log\{[A^{2-}] / [HA^-]\}$

At 3/4 the equivalence point $[A^{2}] = [HA^{-}]$

hence, $(pH)_{3/4} = pK_2$.

A tribasic acid like phosphoric acid dissociates in three steps :

$$H_3PO_4 \rightleftharpoons H_2PO_4^{-} + H^{+} \qquad (K_1)$$

$$H_2PO_4^{-} \rightleftharpoons HPO_4^{2-} + H^{+} \qquad (K_2)$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^{+} \qquad (K_3)$$

where, K_1, K_2 and K_3 are the dissociation constants corresponding to the first, second and third steps of dissociation respectively. Since both ratio K_1/K_2 and K_2/K_3 are greater than 10^4, the titration curve against NaOH solution will show three inflexions.

At the first neutralisation point,

$$(pH)_1 = 1/2\ (pk_1 + pk_2)$$

Also, at the half of the first step of neutralisation,

$$(pH)_{1/2} = pk_1$$

Similarly at the second neutralisation point,

$$(pH)_2 = {}^{1}/_{2}\ (pk_2 + pk_3)$$

From the above relations, we can find pk_1, pk_2, and pk_3.

Titration should not be carried out till the third inflexion since the solution by that time becomes too alkaline (pH~10) for the glass electrode to function properly. At this stage some solid $CaCl_2$ / $BaCl_2$ is added to the solution, then the pH of the solution comes down due to the release of H^{+}ion :

$$2HPO_4^{2-} + 3Ca^{2+} \rightleftharpoons Ca_3(PO_4)_2 + 2H^{+}$$

The titration may now be continued to get the third inflexion.

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Preparation of 100 ml (N/10) standard oxalic acid solution:

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

Table III: Determination of volume of 1 drop from burette:

Initial reading	Final reading	Volume of liquid dropped	No. of drops	Volume/1 drop	Mean volume/1 drop

Table IV: Standarization of ~(N/2) NaOH solution using pH meter:

No. of drops of NaOH soln. (n)	Mean no. of drops n_1+n_2/2	pH	ΔpH	Δn	ΔpH/Δn	Volume of NaOH at equivalence point	Strength of NaOH
0							
3							
6							
9							
:							
30							

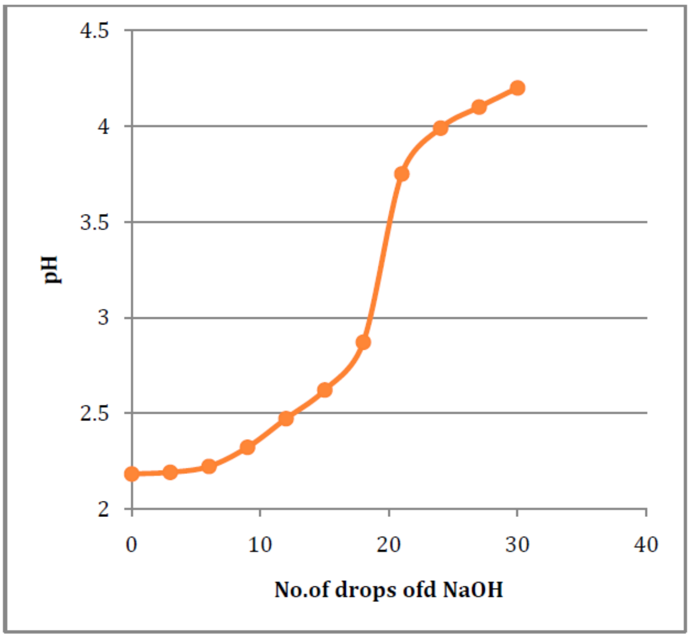
Table V: pH experiment with a known dibasic acid:

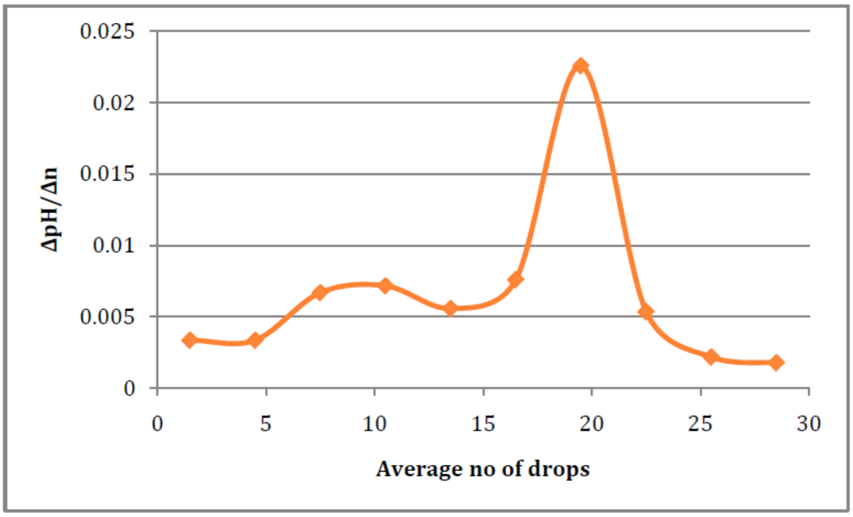
No. of drops of NaOH soln. (n)	Mean no. of drops n_1+n_2/2	pH	ΔpH	Δn	ΔpH/Δn
0					
2					
4					
6					
:					
30					

Table VI: pH experiment with unknown acid:

No. of drops of NaOH soln. (n)	Mean no. of drops n_1+n_2/2	pH	ΔpH	Δn	ΔpH/Δn
0					
2					

4					
5					
:					
18					


4.5
4
3.5
3
2.5
2
pH
0
10
20
30
40
No.of drops ofd NaOH


0.025
0.02
0.015
0.01
0.005
0
ΔpH/Δn
0
5
10
15
20
25
30
Average no of drops