B.Sc. CHEMISTRY LAB MANUAL

4th Semester

Prepared By

Pure & Applied Science Dept.

Chemistry

MIDNAPORE CITY COLLEGE

CHEMISTRY HONOURS
[Choice Based Credit System]
SEMESTER-IV

C8P: Physical Chemistry Lab

Experiment 1: Study of viscosity of unknown liquid (glycerol, sugar) with respect to water

Theory:

From the literature value of viscosity coefficient of water (η_w) at the experimental temperature and the measured specific gravity of solutions of different concentrations we can determine the value of absolute viscosity coefficients of experimental solution of different concentrations. Thus we can study the variation of viscosity coefficient with concentration by plotting a graph of viscosity coefficient vs. concentration. We can also determine concentration of a solution of unknown concentration from the calibration curve.

Apparatus Required:

1) 100ml beaker -2
2) 250ml volumetric flask -1
3) 50ml volumetric flask -4
4) 10ml sp. Gravity bottle -1
5) Viscometer (Time of flow of 10ml of water should be at least 80 secs)
6) 10ml pipette -1
7) Stop watch.

Chemical required:

Sucrose/ Glycerol

Procedure:

1) Prepare a stock solution of 15% (v/v) Glycerol in a 250ml volumetric flask. Then prepare 12%, 9%, 6%, 3% Glycerol solution each of 50ml from the stock solution by exact dilution.
2) Clean the viscometer with chromic acid and wash thoroughly with deionized water. Remove the water completely. Add 10 ml water in the wider limb using a 10ml pipette. Suck up the water in the other limb and allow it to run between two specified marks. Note the time of flow. Remove the water completely. Rinse the viscometer with experimental liquid (start with lowest concentration of experimental solution and then with increasing concentrations] and discard the rinsing. Add 10ml of experimental liquid with pipette , repeat the

procedure and note the time of flow. Note the time of flow for each of the liquid (water, experimental liquids) at least twice.

3) Use a clean dry 10ml specific gravity bottle to determine the specific gravity of the experimental liquids at room temperature. Record the temperature.

Experimental Result :

1) Room temperature:
2) Preparation of Glycerol solution of different concentration from the stock (15%) solution.

Concentration of the prepared solution (%)	Volume of 15% Glycerol solution(ml)	Volume of water(ml)
3	10	40
6	20	30
9	30	20
12	40	10

3) **Determination of specific gravity of experimental liquid:**

Weight of empty sp. Gravity bottle (w_1g)	Weight of sp. Gravity bottle+ water (w_2g)	Weight of sp. Gravity bottle+ expt. Solution(w_xg)	Sp. Gravity of the experimental solution $S_x=(w_x-w_1)/(w_2-w_1)$
		w_3=	S_3=
		W_6 =	S_6=
		W_9=	S_9=
		W_{12}=	S_{12}=
		W_{15}	S_{15}=

4) **Determination of viscosity coefficient of experimental liquids:**

Sl. No	Time of flow for fixed volume of liquid (sec.)					
	Water	Glycerol solution				
		3%	6%	9%	12%	15%
(i) (ii)						

Average time of flow	t_w =	t_3 =	t_6 =	t_9=	t_{12} =	t_{15}=

Calculation :

From the literature value of (η_w) at experimental temperature, absolute value of viscosity coefficient of experimental liquids can be determined ,

$$\eta_x = \eta_w S_x \, . \, t_L/t_w \; = [X= 3,6,9,12,15]$$

Graph Plotting

Coefficient of viscosity (poise)					
Concentration of Glycerol solution	3%	6%	9%	12%	15%

Plotting a graph of viscosity coefficient vs. concentration gives a calibration curve from which unknown concentration of glycerol solution can be obtained.

Experiment 2: Determination of partition coefficient for the distribution of I_2 between water and CCl_4.

Theory:

If a solute (soluble in both the solvents) is added to a pair of immiscible solvents then it will distribute itself between the two solvents in a constant temperature and pressure. This is Nernst distribution law. Let C and C be the molar concentration of the dissolved substance (solute) in solvent I and II respectively.Then according to the above law

$$\frac{C_1}{C_2} = K, \text{ at constant temperature and pressure}$$

Where K is a constant, called distribution or partition co-efficient of the dissolved substance between the solvent I and II.

The thermodynamic criterion for the equilibrium of the above system is that the chemical potential, μ_1 of the dissolved substance in solvent I must be equal to its chemical potential μ_2 in solvent II, i.e.,

$$\mu_1 = \mu_2$$

$$\text{or, } \mu_1^*(T,P) + RT\ln a_1 = \mu_2^*(T,P) + RT\ln a_2$$

Where a_1 and a_2 are activities of the dissolved substance in solvent I and II respectively and μ_1^* & μ_2^* are constant temperature and pressure. Then it follows from the relation that

$$\frac{a_1}{a_2} = \text{Constant, at constant temperature and pressure}$$

If the two solutions behave ideally then the activities will be equal to the respective mole fraction (x), so that

$$\frac{a_1}{a_2} = \frac{x_1}{x_2} \approx \frac{C_1}{C_2}$$,if the solutions are dilute.

Then, $\frac{C_1}{C_2}$ = K, at constant temperature and pressure provided the solutions are ideal and dilute and the dissolved substance exists in the same molecular form in the two solvents (and of course the two solvents must be immiscible, otherwise μ_1^* & μ_2^* will depend on the chemical nature of the solvent).

For example if iodine is added to a mixture of water and carbon tetrachloride and is shaken vigorously, at equilibrium, it will distribute itself between the two solvents in a constant ratio of concentration. Concentration of Iodine in each layer is determined by titrating against sodium thiosulphate solution using starch as indicator.

Apparatus required:

1) 250 ml stoppered glass bottles -2
2) 5 ml pipette – 1
3) 25 ml pipette – 1
4) Burette – 1
5) 500 ml glass bottle – 1
6) 250 ml volumetric flask – 1
7) 250 ml conical flask – 2

Chemicals required:

i)Saturated I_2 solution in CCl_4, ii) Pure CCl_4, iii) 10% KI, iv) 1% starch solution, v) $Na_2S_2O_3$.

Procedure:

1) Prepare 250 ml ~ (N/20) $Na_2S_2O_3$ solution.
2) Prepare 250 ml ~ (N/100) $Na_2S_2O_3$ solution by pipetting out 50 ml ~ (N/20) $Na_2S_2O_3$ solution in a 250 ml volumetric flask followed by dilution up to the mark with deionized water.
3) Prepare two sets in 250ml stoppered glass bottle as follows :

Set	Volume of saturated I_2 solution in CCl_4	Volume of CCl_4(ml)	Volume of water(ml)	Total volume(ml)
1	35	15	100	150
2	15	35	100	150

After mixing stopper the bottles properly and shake vigorously for an hour. Allow to settle for 10 minutes so that two layers become clearly separated.

4) Pipette out 25 ml of the aqueous layer carefully from each set (so that no organic layer is taken out) and titrate with ~ (N/100) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time.
5) Pipette out 5 ml of the organic layer carefully from each set (so that no aqueous layer is taken out) in a 250 ml conical flask. Add 25ml water and 10 ml 10% KI solution to it. Shake well by swirling motion and titrate with ~ (N/20) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time.

Experimental result:

1) Room temperature:
2) Preparation of 250ml ~ (N/20) $Na_2S_2O_3$ solution
3) Prepare 250ml ~ (N/100) $Na_2S_2O_3$ solution from ~ (N/20) $Na_2S_2O_3$ solution:
4) Table 1:Titration of solvent layers

Set	Organic layer				Aqueous layer			
	No. of obs.	Vol. of organic layer(ml)	Vol. of ~ (N/20) $Na_2S_2O_3$ solution (ml)	Mean vol.of ~ (N/20) $Na_2S_2O_3$ solution (ml)	No. of obs.	Vol. of aqueous layer	Vol. of ~ (N/100) $Na_2S_2O_3$ solution (ml)	Mean vol. of ~ (N/100) $Na_2S_2O_3$ solution(ml)
1	i.	5			i.	25		
	ii.	5			ii.	25		
2	i.	5			i.	25		
	ii.	5			ii.	25		

Calculation:

If V_1 ml of 250ml ~ (N/20) $Na_2S_2O_3$ solution is required for 5 ml of organic layer and V_2 ml of ~ (N/100) $Na_2S_2O_3$ solution is required for 25 ml of aqueous layer then partition co-efficient K is given by

$$K=\frac{C_1}{C_2}=\frac{\frac{V_1\times(\frac{N}{20})}{5}}{\frac{V_2\times(\frac{N}{100})}{25}}=25(\frac{V_1}{V_2})$$

Set	**Mean vol. of ~ (N/20) $Na_2S_2O_3$ solution(ml) (V_1)**	**Mean vol. of ~ (N/100) $Na_2S_2O_3$ solution(ml) (V_2)**	**$K=25(V_1/V_2)$**	**Mean K**
I.				
II.				

Precautions and suggestions:

Care should be taken during pipetting out different layers so that no mixing occurs. Use bulb pipetizer instead of mouth sucking during pipetting out layers.

Experiment 3: Determination of Keq for KI + I_2 = KI_3, using partition coefficient between water and CCl_4

Theory:

In aqueous solution I_2 and KI from complex as below

$$KI + I_2 = KI_3$$

For which equilibrium constant (K_{eq}) is given by

$$K_{eq} = \frac{[KI_3]_{aq}}{[I_2]_{aq,free}[KI]_{aq,free}} \quad \text{…….. (i) , for dilute solution}$$

This equilibrium constant can be determined by applying Nernst distribution law if the second immiscible organic solvent is so chosen that only one of the reactants or products can be distributed between two layers. In this case CCl_4 is chosen as second solvent in which I_2 is soluble. If distribution or partition coefficient (K_d)of I_2 in CCl_4 and water at a particular temperature is given by

$$\frac{[I_2]_{CCl_4}}{[I_2]_{water}} = K_d$$

Then at equilibrium, concentration of free iodine in aqueous layer,

$$[I_2]_{aq,\ free} = \frac{[I_2]_{CCl_4}}{K_d}$$

$[KI_3]_{aq}$= Total I_2 in aqueous layer $-[I_2]_{aq\ ,\ free}$

$$= [I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}$$

Concentration of free KI in aqueous solution,

$[KI]_{aq,free}$= Total concentration of KI-$[KI_3]_{aq}$

$$= [KI]_{aq,\ total} - \{[I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d} \}$$

Therefore, $K_{eq} = \frac{[KI_3]_{aq}}{[I_2]_{aq,free}[KI]_{aq,free}} = \frac{[I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}}{\left(\frac{[I_2]_{CCl_4}}{K_d}\right)([KI]_{aq,total} - \{[I2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}\})}$

Thus from the knowledge of $[I_2]_{aq,\ total}$, $[I_2]_{CCl4}$, $[KI]_{aq,\ total}$ and K_d, the value of K_{eq} can be determined.

Apparatus required:

1) 250 ml volumetric flask -2
2) Glass bottle -1
3) Burette -1
4) 25 ml pipette -1
5) 10 ml pipette -1
6) 250 ml stoppered glass bottle -2
7) 500 ml conical flask -1
8) 250 ml conical flask -2
9) Watch glass -1

Chemicals required: $K_2Cr_2O_7$, $Na_2S_2O_3$, KI, I_2 solution in CCl_4, 4(N) H_2SO_4, Starch.

Procedure:

1) Prepare 250ml of standard (N/20) $K_2Cr_2O_7$ solution and 250ml of standard (N/20) KI solution by accurate weighing.
2) Prepare 500ml ~ (N/20) $Na_2S_2O_3$ solution.
3) Standardize the (N/20) sodium thiosulphate solution idometrically using starch solution as indicator. Take 25ml of standard (N/20) $K_2Cr_2O_7$ solution in a 500 ml conical flask. Add about 10ml (one test tube) of 10% KI solution and 25ml of 4(N) H_2SO_4 solution. Cover the conical flask with watch glass and keep in dark for about 5 minutes. Add 150ml of distilled water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator.
4) Prepare two sets in dry, clean 250ml stoppered glass (leak proof) bottles:

Set	Volume of (N/20) KI solution(ml)	Volume of I_2 solution in CCl_4(ml)	Volume of water(ml)
I	10	~40	90
II	20	~40	80

Stopper the bottles properly and shake the mixtures thoroughly for 45 minutes and allow to stand till complete separation of layers.

5) Pipette out 10 ml of the organic layer carefully from each set (so that no aqueous layer is taken out) in a 250ml conical flask. Add 25 ml water and 10ml 10% KI solution to it. Shaken well by swirling motion and titrate with standard (N/20) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time. Calculate concentration of I_2 in organic layer.
6) Pipette out 10ml of the aqueous layer carefully from each set (so that no organic layer is taken out), add ~ 40ml water and titrate with standard (N/20) $Na_2S_2O_3$ solution using starch as indicator. Repeat one more time. Calculate total concentration of I_2 in aqueous layer.

7) Calculate the value of K_{eq} using the supplied value of K_d.

Experimental result:

1) Room temperature.
2) Preparation of 500ml ~ (N/20) $Na_2S_2O_3$ solution.
3) Preparation of 250ml standard (N/20) $K_2Cr_2O_7$ solution.
4) Preparation of 250ml standard (N/20)KI solution.
5) Standardization of the prepared $Na_2S_2O_3$ solution:

Vol. of (N/20) $K_2Cr_2O_7$ solution (ml)	Burette reading		Vol. of $Na_2S_2O_3$ used (ml)	Average vol. of $Na_2S_2O_3$ (ml)
	Initial(ml)	Final(ml)		
25ml				
25ml				

Strength of $Na_2S_2O_3$:

6) Preparation of sets:

Set	Volume of (N/20) KI solution (ml)	Volume of I_2 solution in CCl_4 (ml)	Volume of water (ml)	$[KI]_{aq,total}$

7) Titration of solvent layers:

Set	Organic Layer				Aqueous Layer			
	No. of Obs.	Vol. of organic layer (ml)	Vol. of standard (N/20) $Na_2S_2O_3$ solution (ml)	Mean vol. of standard (N/20) $Na_2S_2O_3$ solution [v_{org}(ml)]	No. of Obs.	Vol. of aqueous layer (ml)	Vol. of standard (N/20) $Na_2S_2O_3$ solution (ml)	Mean vol. of standard (N/20) $Na_2S_2O_3$ solution [v_{aq}(ml)]
I	i	10			i	10		
	ii	10			ii	10		
II	i	10			i	10		
	ii	10			ii	10		

Calculation:

For Set I :

Concentration of I_2 in organic layer, $[I_2]_{CCl_4} = \frac{Mean\ vol.of\ Na_2S_2O_3(V_{org}) \times \text{its strength}}{10}$

Total concentration of I_2 in aqueous layer, $[I_2]_{aq,\ total} = \frac{Mean\ vol.of\ Na_2S_2O_3(Vaq) \times its\ strength}{10}$

Similarly for set II calculate $[I_2]_{CCl_4}$ and $[I_2]_{aq,\ total}$.

Calculate k_{eq} for set I and set II using the relation,

$$K_{eq} = \frac{[I_2]_{aq,total} - \frac{[I_2]_{CCl_4}}{K_d}}{\left(\frac{[I_2]_{CCl_4}}{K_d}\right)\left([KI]_{aq,total} - \left\{\left[I_2\right]_{aq,total}\frac{[I_2]_{CCl_4}}{K_d}\right\}\right)}$$

Experiment 4: Conductometric titration of an acid (strong, weak/ monobasic, dibasic) against base strong.

Theory:

The conductance of an electrolyte solution depends on the mobility and concentration of each type of ions present in the solution. Any reaction which is associated either with replacement of one kind of ion by another of different mobility or with a charge I ionic concentration will be associated with a change in conductance of the reaction mixture. For such reaction gradual addition of one of the reactant to the other will result in a change of conductance in particular manner (depending on the nature of the reaction) up to equivalence point and in different manner after equivalence point. Then equivalence point corresponds to the break in titration curve obtained on plotting the conductance against the volume of the added substance (titrant).The conductance should be measured in a conductivity cell placed in a thermostat (to avoid change in conductance due to change in temperature). The titrant used should be many times stronger than the solution to be titrated to avoid change in conductance due to dilution .To avoid change in conductance due to change of electrolyte concentration resulting from electrolysis with direct current, measurement of conductance should be done using Alternating current based on Wheatstone Bridge principle. The electrodes used must be platinized (to avoid polarization).

Different cases of Conductometric titration:

1) Strong acid vs. strong base:

Let us consider a strong acid (e.g.HCl) is titrated by a strong base (e.g. NaOH). Here the reaction involved is

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

In this reaction H^+ ions are replaced by Na^+ ions of lower mobility. Therefore conductance of the reaction mixture will gradually decrease linearly up to equivalence point and after equivalence point the conductance will increase linearly due to excess of added electrolyte (NaOH) . The nature plot conductance vs volume of NaOH added is shown in the Figure-7.1, where intersection of two straight lines (say O) represents the equivalence point.

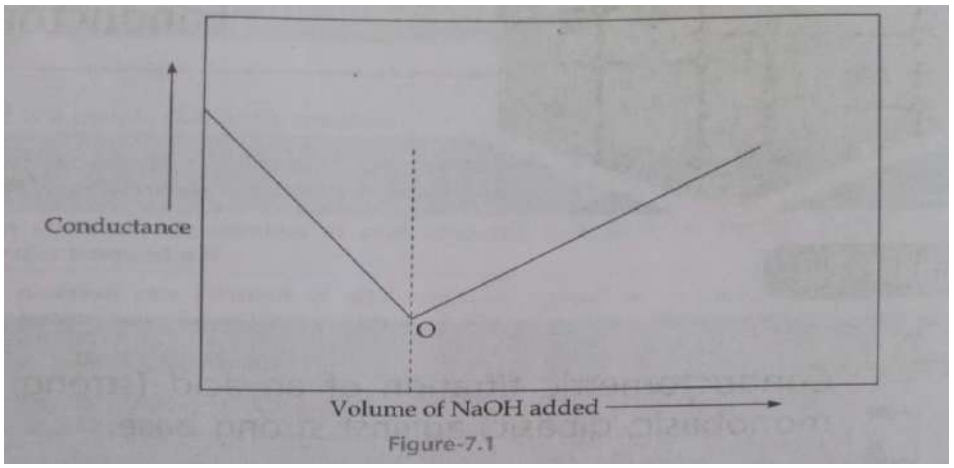


Figure-7.1

2) Weak acid (monobasic, dibasic) vs. strong base:

a) Titration of weak monobasic acid (CH_3COOH) by strong base (NaOH):

Here the reaction involved is

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ + Na^+ + OH^- \rightarrow Na^+ + CH_3COO^- + H_2O$

Initially H^+ ions (resulting from slight dissociation of CH_3COOH) are replaced by Na^+ ions of lower mobility. Due to this and also suppression of dissociation, conductance of reaction mixture initially slightly decreases. After appreciable addition of NaOH the conductance of reaction mixture will gradually increase up to equivalence point due to formation of highly ionized $CH_3COO^-Na^+$. After equivalence point the conductance will further increase at a different rate. The break in titration curve (Figure7.2) indicates the equivalence point.

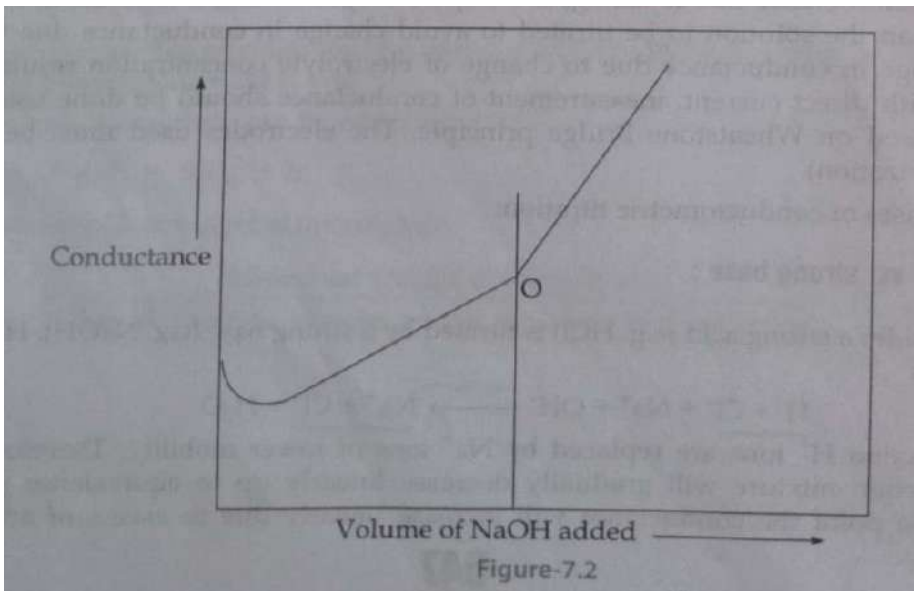
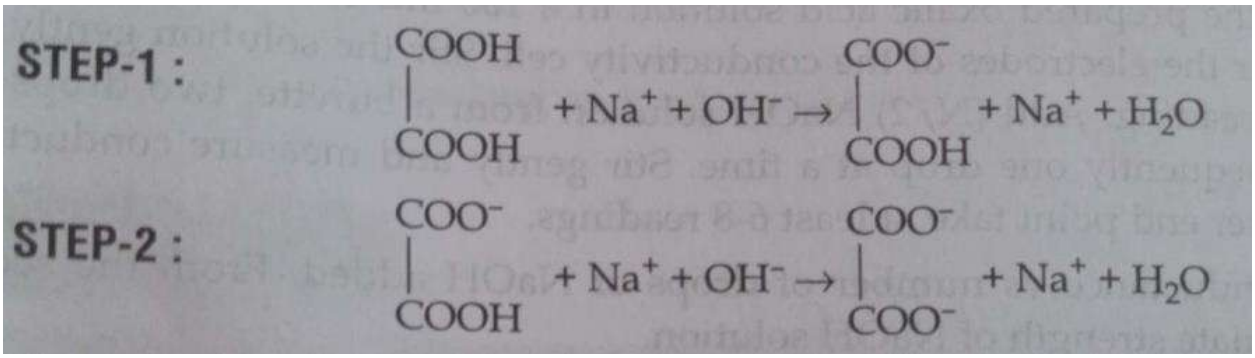


Figure-7.2

b) Titration of weak dibasic acid (Oxalic) by strong base (NaOH):

Here the reaction involved is



Oxalic acid is a dibasic acid and its $pk_2 > pk_1$. Therefore initially up to first equivalence point it will act as a relatively strong acid and conductance of the reaction mixture will gradually decrease linearly up to 1st equivalence point (O) (Figure 7.3) (because H^+ ions are replaced by $HC_2O_{4^-}$ ions of lower mobility). Then conductance increases slowly up to 2nd equivalence point due to increase of $C_2O_4^{2-}$ ions with gradual addition of NaOH. After 2nd equivalence point (O_1) conductance will increase rapidly due to excess of added electrolyte(NaOH).

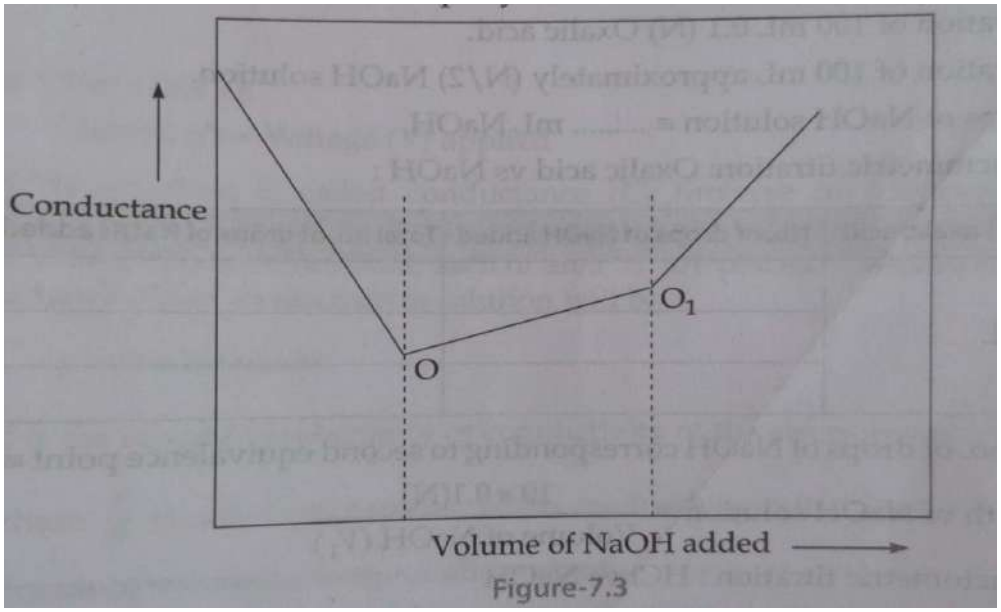


Figure-7.3

Apparatus required:

1) Conductivity meter
2) 100ml beaker
3) Burette (50ml), pipette (10ml) -1
4) 100ml volumetric flask -1
5) 250ml Glass bottle -3

Chemicals required:

Oxalic acid, NaOH, Acetic acid, HCl

Procedure:

1) Prepare 100ml ~(N/2) NaOH solution.
2) Prepare 100ml (N/10) Oxalic acid solution by exact weighing in a volumetric flask.
3) Prepare 100ml ~(N/10) HCl and 100ml ~(N/10) acetic acid solution.
4) Take the NaOH solution in a burette. Determine the volume of 50 drops and calculate the volume of one drop.
5) Standardize the ~(N/2) NaOH solution in the following way. Pipette out 10ml of the prepared oxalic acid solution in a 100ml beaker, add sufficient distilled water to cover the electrodes of the conductivity cell. Stir the solution gently and take the conductance reading. Add (N/2) NaOH solution from a burette, two drops at a time initially and subsequently one drop at a time. Stir gently and measure conductance after each addition. After end point take at least 6-8 readings.
6) Draw the graph of conductance vs number of drops of NaOH added . From the second equivalence point calculate strength of NaOH solution.
7) Standardize the prepared HCl and acetic acid solution following the procedure of step 5.
8) From the graph of conductance vs number of drops of standard NaOH added, calculate strength of prepared HCl and acetic acid solution.

Experimental result:

1) Room temperature.
2) Preparation of 100ml 0.1(N) Oxalic acid.
3) Preparation of 100ml approximately (N/2) NaOH solution.
4) 50 drops of NaOH solution=…… ml NaOH.
5) Conductometric titration: Oxalic acid vs NaOH:

Volume of (N/10) oxalic acid	No. of drops of NaOH added	Total no, of drops of NaOH added	Conductance (mho)
10ml			

Total no. of drops of NaOH corresponding to second equivalence point≡…..ml NaOH(V_1).

Strength of NaOH solution = $\frac{10\times0.1(N)}{\text{Volume of NaOH}(V1)}$

6) Conductometric titration : HCl vs NaOH

Volume of HCl	No. of drops of NaOH added	Total no. of drops of NaOH added	Conductance(mho)
10ml			

Calculate strength of HCl in a similar way as step 5.

7) Conductometric titration: Acetic acid vs NaOH

Volume of acetic acid	No. of drops of NaOH added	Total no. of drops of NaOH added	Conductance(mho)
10ml			

Calculate strength of Acetic acid in a similar way as step 5

Precautions and Suggestions:

1) Add NaOH solution from a burette, two drops at a time initially and subsequently one drop at a time.
2) Stir gently before taking each conductance reading.

Experiment 5: Study of saponification reaction conductometrically

Theory:

Saponification of ester refers to the aqueous alkaline hydrolysis of any type of ester. As an example saponification of methyl acetate can be represented as

$$CH_3COOCH_3 + OH^- \rightarrow CH_3COO^- + CH_3OH$$

The rate of the reaction, $R = \frac{d[ester]}{dt} = k[ester][OH^-]$, i.e.

the overall kinetic order of the reaction is two.

If 'a' be the initial concentration of ester and 'x' be the concentration of ester reacted at time t then the concentration of unreacted ester is (a-x) . For equal initial concentration of both the reactants we have,

$-\frac{d(a-x)}{dt} = k(a-x)^2$, Where k is the second order rate constant with unit of $mol^{-1}L.s^{-1}$

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

Integrating this equation by imposing boundary condition , at t=0, x=0, we have,

$$\frac{x}{(a-x)} = k \text{ at}$$

The course of the reaction can be monitored by measuring conductance of the reaction mixture with time. In this case the conductance of the reaction mixture decreases with time as the OH^- ions are replaced by CH_3COO^- ions of lower mobility . Therefore from the measured conductance value the relative amounts of the ions present and hence the extent of reaction can be predicted. If C_0, C_t, and $C\infty$ are the values of conductance at time t=0, t=t and t=∞ respectively, then

$$a \propto (C\infty - C_0)$$

$$(a-x) \propto (C\infty - C_t)$$

$$x \propto (C_t - C_0)$$

Substituting in equation (i) we get, $\frac{C_0 - C_t}{C_t - C_\infty} = k$ at

Plot of $\frac{C_0-C_t}{C_t-C_\infty}$ vs t should yield a straight line passing through the origin with a slope 'ka'. From the known value of 'a', the rate constant for the saponification reaction, k can be calculated.

Apparatus required:

1) 100ml vol. flask -5
2) 250ml conical flask -1
3) 100ml beaker -1
4) 500ml glass bottle -1
5) Burette -1
6) Pipette 25ml -2
7) Pipette 10ml -1
8) Pipette 1ml -1

Chemicals required:

Oxalic acid, NaOH, Acetic acid, Phenolphthalein, Methyl acetate

Procedure:

1) Prepare 100ml of ~(N/10) oxalic acid solution by exact weighing.
2) Prepare 250ml of ~(N/10) NaOH solution. Standardize this NaOH solution against 10ml standard oxalic acid solution.(Use Phenolphthalein).
3) Dilute the standardized NaOH solution to prepare exact (M/60)NaOH solution of volume 100ml using deionized water.
4) Prepare 100ml of a ~(N/10) acetic acid (HAc) solution. Standardized 10ml of it against the standardized ~(N/10) NaOH solution (Use Phenolphthalein). From the standardized solution prepare 100ml exact (M/60) HAc solution by proper dilution.
5) Take a 100ml volumetric flask with about 50ml of deionized water. Transfer into this exactly 1.0ml of pure methyl acetate, using a 1ml graduated pipette, and make up the volume with deionized water. Estimate the concentration of the solution in molarity using the following data:

Molecular weight of methyl acetate = 74.08

Density of the supplied methyl acetate at room temperature (t^0C)

$$=0.932- (t-20)\times 1.25 \times 10^{-4} \text{ g/ml}$$

Prepare 100ml exact (M/60)methyl acetate solution from this standard methyl acetate solution by proper dilution with deionized water.

6) Prepare 50ml exact (M/120) NaOH solution from exact (M/60) NaOH solution by proper dilution (use a 25ml pipette) with deionized water and note its conductance as C_0.
7) Mix 25ml each of (M/60) NaOH and (M/60) HAc solutions and note its conductance as $C\infty$.
8) Take 25ml (M/60) methyl acetate and add 25ml (M/60) NaOH solution to it. Note the time of half – discharge of the pipette and homogenize the mixture. Measure the conductance (C_t) of the solution at intervals of about 1 minute. Take at least 15 reading.
9) Plot $(C_0-C_t)/(C_t-C\infty)$ versus time to obtain the rate constant of the reaction at room temperature.

Experimental result:

1) Room temperature.
2) Preparation of 100ml 0.1 (N) oxalic acid.
3) Preparation of 250ml approximately 0.1(N) NaOH solution.
4) Standardisation of NaOH solution against standard oxalic acid solution.

Volume of oxalic acid (ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of NaOH solution.

5) Preparation of 100ml exact (M/60) NaOH solution.
6) Preparation of 100ml $\sim\left(\frac{N}{10}\right)$ acetic acid solution.
7) Standardisation of HAc solution against standard NaOH solution.

Volume of HAc (ml)	Burette reading		Volume of NaOH used (ml)	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of HAc solution.

8) Preparation of 100ml exact (M/60) HAc solution.
9) Preparation of 100ml exact (M/60) methyl acetate solution.

10) Measurement of C_0 and $C\infty$

C_0=conductance of (M/120) NaOH solution.

$C\infty$ = conductance of (M/120) sodium acetate solution.

11)Recording of conductance data for saponification reaction.

Time (t) in minute	Conductance (C_t) (mho)	C_0-C_t(mho)	C_t-$C\infty$ (mho)	(C_0-C_t)/(C_t-$C\infty$)

Conclusion:

Plot of $\frac{C_0-C_t}{C_t-C_\infty}$ vs t gives a straight line passing through the origin. From the graph slope = ka.

Or, k=Slope/a, where 'a' is initial concentration of reactants = (M/120).

Experiment 6: Verification of Ostwald's dilution law and determination of Ka of weak acid.

Theory:

Electrolytes obey Ohm's law i.e.,

Current (I) ∝ Voltage (V) applied

The proportionality constant is called conductance (C) [inverse of resistance (R)] of the conductor concerned. The conductance of an electrolyte solution is measured with the help of a conductivity cell. If two parallel electrodes, each of area 'A' are placed 'I' distance apart then the measured conductance (C) of an electrolyte solution will be

C= $\frac{1}{R} = \frac{1}{\rho}\frac{A}{l}$, ρ is the resistivity

= k $\frac{A}{l}$, k is the specific conductance or conductivity of the electrolyte solution.

Or, k = C$\frac{l}{A}$, Where $\frac{l}{A}$ is called cell constant of the conductivity cell

i.e., Specific conductance = Conductance × Cell constant

The specific conductance (k) of an electrolyte solution is its conductance when unit volume of the solution is placed between two parallel electrodes each of unit area and set unit distance apart. In C.G.S. its unit is ohm^{-1} cm^{-1}.

Cell constant of a conductivity cell is determined by measuring the conductance of an electrolyte solution of known specific conductance at the experimental temperature within the same conductivity cell.

Equivalent conductance (λ) of an electrolyte solution is its conductance associated with a definite volume of the solution containing 1 gm equivalent of the electrolyte placed between two large electrodes set unit distance apart. Therefore,

Equivalent conductance (λ) = Specific conductance (k) × volume of the solution in cm^3 containing 1 gm equivalent of the electrolyte

Unit of 'λ′ in CGS in ohm^{-1}cm^{2}g equi^{-1}.

Equivalent conductance of a weak electrolyte will increase with dilution and this is mainly due to increase n degree of dissociation, the variation of ionic mobility with dilution being insignificant due to low concentration of the ions.

Let α be the degree of ionization of a weak acid HA at concentration C equivalent/lit.

Then at equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

The dissociation constant or ionization constant (K_a) can be represented as

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If equivalent conductance of the weak electrolyte at concentration/ lit and at infinite dilution are λ and λ_0 respectively then,

$$\alpha = \frac{\lambda}{\lambda_0}$$

$$\text{so, } K_a = \frac{C(\lambda/\lambda_0)^2}{1-\frac{\lambda}{\lambda_0}}$$

$$\text{or, } 1-\frac{\lambda}{\lambda_0} = \frac{C\lambda^2}{K_a{\lambda_0}^2} \qquad \text{or, } \frac{1}{\lambda} = \frac{1}{\lambda_0} + \frac{\lambda C}{{\lambda_0}^2 K_a}$$

This is known as Ostwald dilution law. The plot of $\frac{1}{\lambda}$ vs. λC will be a straight line with a positive intercept $\frac{1}{\lambda_0}$ from which λ_0 can be calculated. From the slope $\frac{1}{{\lambda_0}^2 K_a}$, K_a can be calculated using the temperature corrected literature value of λ_0.

Apparatus required:

1) 100ml vol. flask -3
2) 250ml conical flask -1
3) 100ml beaker -2
4) 500ml glass bottle -2
5) Burette -1
6) Pipette 25 ml -2
7) Pipette 10ml -1
8) 250ml vol. flask -2

Chemicals required:

Oxalic acid, Acetic acid, NaOH, KCl, Phenolphthalein

Procedure:

1) Prepare 100ml ~(N/10) oxalic acid solution by accurate weighing.
2) Prepare approximately 250ml of ~(N/10) NaOH solution and standardize the NaOH solution against the prepared standard oxalic acid solution.(use phenolphthalein).
3) Prepare 250ml of ~(N/10) acetic acid solution in conductivity water and standardize the solution against the standard NaOH solution (use phenolphthalein).
4) Prepare 250ml ~ 0.1 (N) [slightly higher than 0.1 (N) KCl solution by accurate weighing and prepare 100ml of an exact 0.1 (N) KCl solution by proper dilution. Prepare 100ml of an exact 0.01 (N) KCl from the exact 0.1 (N) KCl solution. Determine the cell constant of the conductivity cell using the exact 0.1 (N) KCl and the prepared exact 0.01 (N) KCl solution .With the help of the literature value of specific conductances of these solutions at room temperature, calculate the mean value of cell constant and use it subsequently. Measure the conductance of conductivity water also.
5) Prepare 250ml, exact (N/50) weak acid solution from the standardized solution using conductivity water. With the help of 25ml pipette, take 50ml of this solution in the clean and dry conductivity cell and measure its conductance.
6) Use the same 25ml pipette to take out 25ml of the (N/50) weak acid solution from the conductivity cell. Pipette out 25ml of the conductivity water into the conductivity cell to make the solution exactly (N/100) in situ. Mix the solution well by careful swirling (so that no solution comes out). Measure the conductance and note it as that of exact (N/100) weak acid solution.

Separate pipettes for weak acid solutions and conductivity water may be used.

7) Follow the procedure of step (6) to prepare in situ exact (N/200), (N/400), (N/800), and (N/1600) weak acid solutions in steps and note their conductances.
8) Calculate the equivalent conductivities of the diluted solutions of the weak acid using the mean value of cell constant. Apply corrections for specific conductance of conductivity water.
9) From the plot of $1/\lambda$ versus (λC) calculate the λ_0 from the intercept and from the temperature corrected literature value of ion conductances. Calculate K_a and pk_a of the weak acid from the slope using the temperature corrected literature value of λ_0.

Experimental result:

1) Room temperature.
2) Preparation of 100ml 0.1(N) oxalic acid.
3) Preparation of 250ml approximately 0.1(N)NaOH solution.
4) Standardisation of NaOH solution against standard oxalic acid solution:

Volume of oxalic acid (ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of NaOH solution: …….

5) Preparation of 250ml ~(N/10) acetic acid solution:

6) Standardisation of acetic acid solution against standard NaOH solution :

Strength of acetic acid solution:

Volume of acetic acid solution(ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

7) Preparation of 250ml exact (N/50) acetic acid solution.

8) Preparation of 250ml ~0.1 (N) [slightly higher than 0.1 (N) KCl solution.
9) Preparation of 100ml exact 0.1 (N) KCl solution and preparation of exact 0.01 (N) KCl .
10) Determination of cell constant:

Concentration of KCl solution	Conductance (mho)	Specific conductance ($mho.cm^{-1}$)	Cell constant (cm^{-1})	Mean cell constant (cm^{-1})
0.01(N)				
0.1(N)				

11) Determination of equivalent conductance of different acetic acid solutions:

Concentration of acetic acid solution	Observed conductance (mho)	Corrected specific conductance ($mho.cm^{-1}$) {Observed conductance-Conductance of conductivity water) × mean cell constant}	Equivalent conductance (λ) ($mhocm^2eq^{-1)}$	$1/\lambda$ ($mho^{-1}cm^{-2}eq$)	$\Lambda c(mhocm^{-1})$

The plot of $\frac{1}{\lambda}$ vs λC will be a straight line with a positive intercept $\frac{1}{\lambda_0}$ from which λ_0 can be calculated.

From the slope $\frac{1}{\lambda_0{}^2 K_a}$, K_a can be calculated using the temperature corrected literature value of λ_0.

Temperature corrected literature value of $\lambda_0 = \lambda_t^0 (H^+) + \lambda_t^0 (OAc^-)$

$$\lambda_t^0 (H^+) = \lambda_{25}^o [1+1.42\times 10^{-2} (t-25)]$$

$$\lambda_t^0 (OAc^-) = \lambda_{25}^o [1+0.02 (t-25)]$$

C9P: Inorganic Chemistry Lab

Complexometric titration

1. Determination of Hardness of water

Objective: Measure (1) Total hardness and (2) Calcium hardness using dye indicators

Background:

Hard Water: Hard waters are generally considered to be those waters that require considerable amounts of soap to produce foam and that also produce scale in water pipes, heaters, boilers and other units in which the temperature of water is increased. Hard water are appropriate for human consumption similar to that as soft waters, however it produces adverse actions with soap and thus their use for cleaning purposes is unsatisfactory and thus their removal from water is required. Hardness of waters varies from place to place. In general, surface waters are softer than ground waters. Waters are commonly classified based on degree of hardness (Table 1):

Table 1. Classification of hardness types

Hardness (mg/L)	Degree of hardness
0-75	Soft
75-100	Moderately hard
150-300	Hard
>300	Very hard

Hardness:

Hardness is caused by polyvalent metallic cations, though the divalent cations, such as calcium and magnesium cations are usually the predominant cause of hardness. In addition, hardness is also caused by Fe^{2+} and Mn^{2+} ions. For example, when hard water is heated, Ca^{2+} ions react with bicarbonate ($HCO3^-$) ions to form insoluble calcium carbonate ($CaCO_3^-$) (Eq. 1).

This precipitate, known as *scale,* coats the vessels in which the water is heated, producing the mineral deposits on your cooking dishes. Equation 2 presents magnesium hardness.

$$Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} \longrightarrow CaCO_{3(s)} + H_2O + CO_2 \quad (1a)$$

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Mg(OH)_{2(s)} \quad (1b)$$

Total hardness is defined as the sum of the calcium and magnesium concentrations, bothexpressed as calcium carbonate in mg/L. When hardness (numerically) is greater than the sum of carbonate and bicarbonate alkalinity, amount of hardness equivalent to the total alkalinity iscalled "Carbonate hardness". Carbonate hardness (mg/L) = Alkalinity (2a) When alkalinity > Total hardness:

Carbonate hardness (mg/L) = Total hardness (2b)

The amount of hardness in excess of this is called "Non-carbonate hardness (NCH)". Theseare associated with sulfate chloride, and nitrate ions. It is calculated using Eq (2c):

NCH (mg/L) = Total hardness-Carbonate hardness (2c)

Determination of Hardness:

Hardness is expressed as mg/L CaCO3. The first method is calculation based method and the second method is titration method using EDTA.

(i) **Calculation method**

For this method, concentration of cations should be known and then all concentrations are expressed in terms of CaCO3 using Eq. 3:

Hardness (in mg/L as $CaCO_3$) = [M^{2+} (in mg/L) × 50]/ (E.Wt. of M^{2+}) (3)

Where: M^{2+} = mass of divalent ions (mg/L) and E.Wt. = Equivalent weight of divalent ions (g/mole)

Example: If in a sample, 15 mg/L $Ca^{2+}$are present, hardness is given by

Hardness (in mg/L as $CaCO_3$) = [mass of Ca^{2+} (in mg/L) × 50]/ (E.Wt. of Ca^{2+})

Here, E.Wt. of Ca^{2+} = (40g/mole)/2=20 g/mole

So, Hardness due to calcium ions = [15 mg/L × 50]/ (20) = 37.5 mg/L $CaCO_3$

(ii) **EDTA Titrimetric Method:**

This method uses ethylenediaminetetracetic acid (EDTA), chelating agents, which forms complex ions with Ca2+and Mg2+ and other divalent ions causing hardness (Eq. 4a):

M^{2+} + EDTA: [M.EDTA]complex (4a)

The successful use of EDTA for determining hardness depends on presence of an indicator which can show presence of excess EDTA in solution or when all the ions present in solution have been complexed. Eriochrome Black T (EBT) (blue color solution) serves as an excellent

indicator to show when all hardness ions have been consumed. When small amount of EBT is added to hard water with pH>10, it combines with Ca^{2+} and Mg^{2+} ions to form weak complex ions (wine-red color solution) (Eq. 4b):

M^{2+} + Eriochrome Black T: [M.Ericochrome Black T]complex (4b)

During the titration with EDTA, all free hardness ions are complexed as per Eq. 4a and subsequently, EDTA disrupts the wine red complex as it can form a stable complex with the hardness ions. At this stage, solution color changes from red wine color to blue color, indicating the end of the titration.

Lab Procedure:

Reagents: Buffer solution; EDTA Titrant; EBT

1. Measure Ca-Hardness and Total Hardness by titration as described below. Use adifferent sample for each measurement.

2. Total Hardness: Take 100 ml of the sample and add 2 ml buffer solution in it and add 2-3 drops of Black T. Titrate it with standard EDTA solution (with continuous stirring) until the last reddish colour disappears. At the end point the solution turns blue. Note down the volume used. Calculate Hardness as follows:

Hardness (in mg/L as CaCO3) = (V× N × 50 ×1000) / (SV) (5)

Where: V = volume of titrant (mL); N = normality of EDTA; 50 = equivalent weight of CaCO3; SV = sample volume (mL)

3. Ca-Hardness: Take 50 ml of the sample and add 1 ml Sodium Hydroxide solution (8%)in it and add pinch of Mercurex Powder. Titrate with standard EDTA solution until thelight pink colour of solution converts into light blue color.

2. Complexometric titration: Analysis of Zinc [Zn(II)]

Objective:

Complexometric volumetric titrations with EDTA (**e**thylene**d**iamine**t**etraacetic **a**cid) will be performed. The comprehension and skills learned will be transferable to other laboratory and workplace situations.

- A primary-standard zinc ion solution will be prepared from primary-standard zinc metal.
- A supplied EDTA solution will be standardized using the primary-standard zinc ion solution.
- The secondary standard EDTA solution will be employed to determine the zinc content of a Supplied sample.

A primary-standard zinc metal ion solution was prepared by dissolving 0.2619 g of primary-standard-grade zinc metal in dilute HCl and adding distilled water to the mark in a 250 mL (0.2500 L) volumetric flask. Zn MW = 65.37 g / mol

Calculate the molarity of the zinc metal ions in the solution. State the value to 5 places after the decimal point.

$$\text{Molarity (M)} = \frac{\text{solute concentration in moles per litre (mol / L)}}{} = \frac{\text{amount of solute (mol)}}{\text{total solution volume (L)}}$$

$$\text{Molarity (M)} = 0.2619\ \text{g Zn} \times \frac{1\ \text{mol Zn}}{65.37\ \text{g Zn}} \times \frac{1}{0.2500\ \text{L}}$$

$$\textbf{Molarity of Zinc Ion} = 0.0160257\ \text{mol / L Zinc Ion} = \underline{0.01603}\ \text{M}$$

Preparation of Glassware and Apparatus:

The following clean glassware and laboratory apparatus is required for the experiment:

For each student:

➢ a 50 mL buret and its stand	➢ a weighing bottle and its lid*
➢ a plastic buret funnel	➢ all available erlenmeyer flasks
➢ a 10 mL transfer pipet	➢ a small watch glass to fit a small beake
➢ a small funnel	➢ a 250 mL volumetric flask and its stopper
➢ two small beakers	➢ a glass stirring rod
➢ a spatula	➢ a rubber pipet squeeze bulb

* The instructor may direct you to use a clean, dry weighing boat instead of the weighing bottle.

A-1. Clean the glassware and apparatus if necessary with a 1 % solution of detergent in warm water. See Cleaning and Drying of Glassware on page Error! Bookmark not defined. Rinse the cleaned glassware and apparatus with tap water and then with distilled water.To avoid breakage, do not leave any glassware standing in an unstable position.

A-2. Dry the spatula (and the weighing bottle and its lid if used) in the oven at 110 or 120 ºC for 15 minutes. Do not allow the bottle and lid to vacuum seal.

A-3. Carefully remove your spatula, your weighing bottle, and its lid from the oven on to a heat proof pad. Take them to your bench position and allow them to cool to room temperature before using them.

B. Preparation of a Primary Standard Solution of Zinc Ions

B-1. Label one of your clean small beakers in such a way that you will be able to identify it later in a crowd of other beakers.

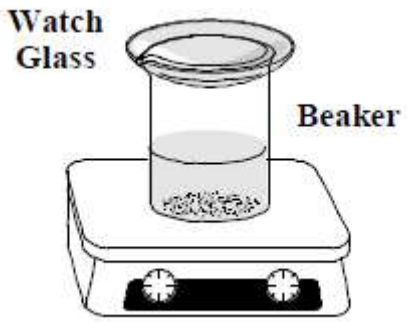
B-2. Use a top-loading balance to place 0.22 - 0.28 g of primary-standard zinc metal into your clean dry container. Do not transfer solid over any balance.

B-3. Use an analytical balance to weigh the container plus the zinc metal. Transfer as much as possible of the zinc metal into your labeled beaker. Reweigh the container and solid residue of the analytical balance.

B-4. Record the initial and final mass values in ink to four places after the decimal point in Table B in the DATA TABLES AND REPORT section. This is a weighing by difference.

B-5. Add distilled water to about the 20 mL mark of the labeled beaker with the zinc metal in it.

B-6. Be sure the fume hood fan is operating. In the fume hood use a graduated cylinder ora dispenser as instructed to measure about 10 mL of 6 M hydrochloric acid (dilute HCl) and



carefully add this to the zinc metal in your beaker. (Caution: hazardous).

B-7. Stay in the fume hood. A reaction will occur, and bubbles of hydrogen gas will be seen. Cover the beaker with your clean watch glass. Set the covered beaker and its contents to heat gently on one of the hot-plates set in the fume hood. The heat control must be on a low setting. Do not boil away all of the liquid.

B-8. If the zinc metal does not fully dissolve or ceases to react with the acid (if gas bubbling stops), add small portions (2 to 3 mL) of acid until it is all dissolved. The resulting solution of zinc ions may then be removed from the fume hood.

B-9. Use a clean funnel and a wash bottle to transfer the solution quantitatively from the beaker, into your clean 250 mL volumetric flask. Rinse the beaker and the funnel with distilled water, adding the wash water to the volumetric flask.

B-10. Add distilled water to the flask to about one cm below the mark line. Fill the flask to the mark line using a dropper pipet.

B-11. Stopper the flask with a clean stopper. Hold the stopper in place withone hand. Turn the flask over slowly at least 17 times to ensure that the solution is completely uniform.

B-12. Clean your small beaker if necessary for the next part of the procedure.

C. Buret Preparation

C-1. Take your buret stand and your 50 mL buret to your bench station. You should also have a clean 10 mL volumetric transfer pipet, a plastic buret funnel if needed, two small beakers and at least three erlenmeyer flasks. Dry the outside of the buret, the pipet, the beakers and the flasks.

C-2. Assemble the buret securely, and check that the buret tap is working. Drain the buret and pipet upside down in the buret stand. Check that the inner walls of the buret and the transfer pipet are clean and that the capillary tips are not broken or plugged. It is not possible to do a good analysis with dirty glassware.

C-3. Label one clean small beaker to be used for the supplied EDTA solution. Into this beaker, pour about 20 mL of the EDTA solution, using the beaker volume markings. Record the code number of the EDTA solution in Table E in the DATA TABLES AND REPORT section.

C-4. Rinse the inside walls of the beaker with the EDTA solution. Pour the solution into the buret, rinsing the inner walls of the buret with the solution. Drain some of the solution out through the tip of the buret into a waste beaker or flask. Rinse the small plastic buret funnel also, if it is to be used.

C-5. Repeat the entire rinse process and collect the rinse solution again. The third time, take a larger volume in the beaker and fill the buretto near the 0.00 mL mark, clearing the tip of air bubbles. Discard all of the rinse solution portions collected in the waste vessel into a sink with the cold water tap running.

D. Pipet Preparation and Pipetting of Portions of the Standard Zinc Solution

D-1. Label another clean small beaker to be used with your standard zinc solution from the 250 mL volumetric flask. Rinse this beaker with about a 20 mL volume of zinc solution from your volumetric flask. Use this portion of the solution to rinse out the 10 mL transfer pipet as well. Collect these rinse portions in a waste beaker or flask.

D-2. Repeat the rinsing and collect the rinse portions again. On the third refill, take about 40 mL to 50 mL of the zinc solution into the beaker. Discard all of the rinse solution portions collected in the waste vessel into a sink with the cold water tap running.

D-3. The Erlenmeyer flasks for the titrations must be clean but the insides need not be dry. Check that your squeeze bulb is clean and dry inside.

D-4. Transfer by pipet one 10.00 mL portion of the standard zinc solution from its beaker into each of three clean Erlenmeyer flasks. Remember to wipe off the tip of the pipet before the transfer. If you are unsatisfied with your pipetting technique in any transfer, discard the sample in that Erlenmeyer flask, rinse the flask well with distilled water, and do it again.

Never transfer by pipet directly from a volumetric flask or a storage bottle.

Always use a beaker or some other intermediate vessel.

D-5. Add to each erlenmeyer flask:

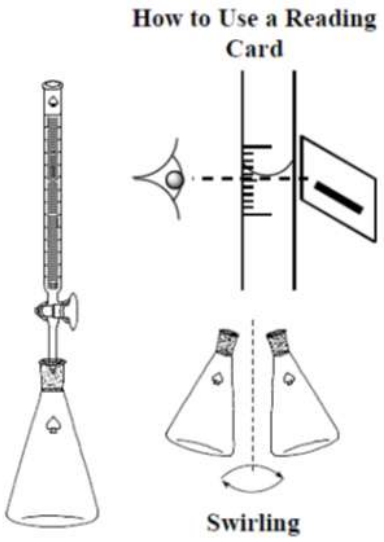
a. Distilled water approximately to the 20 mL mark.

b. About 5 mL of pH 5.5 buffer solution.

c. Three (3) drops of xylenol orange indicator solution.

D-6. Mix well. The indicator colour should be red at this point. Xylenol orange is red when complexed with zinc at pH 5.5. It is yellow when it has been displaced from the zinc by EDTA at the end-point of the titration.

E. Standardization of an EDTA Solution.



E-1. Using a buret reading card, or otherwise, read thestarting volume in the buret to 2 places after thedecimal point to the nearest 0.05 ml. Record thevalue in Table E in the DATA TABLES ANDREPORT section (Start Volume of Trial 1).E-2. Titrate the first sample flask slowly with smalladdition volumes of the EDTA solution. Place the tipof the buret 1 or 2 cm down into the opening of theflask to avoid any accidental loss of solution. Swirl theflask gently to mix the solutions.E-3. When a yellow colour begins to appear in the flask,decrease the volumes of the additions. Add solutionslowly, one or two drops at a time, washing down theinside walls of the flask and the buret tip with a streamof distilled water from your wash bottle from time totime.

The end-point colour of the titration is when the red colour changes to yellow.

E-4. Record the final volume reading to 2 places after the decimal point to the nearest 0.05mL in Table E (Final Volume of Trial 1). Determine the titration volume of Trial 1 andrecord this in Table E.E-5. Repeat titrations are expected to have the same titration volume to the end-point. In thefollowing trials you can add all but the final 1 mL rapidly, using the first titration volumeas a guide. Record all volumes in Table E.Continue doing trials until you have three acceptable trial titration volumes within arange of no more than 0.20 mL.

Table E: Standardization of an EDTA Solution

Code of EDTA Solution: _____ Zinc Ion Molarity (Table B): = _____ M

Portion Volume of Zinc Solution = 10.00 mL = 0.01000 L

End-Point Indicator Volume Correction (Indicator Blank)

Final _____ mL - Start _____ mL = _____ mL

Titration Volumes (In Ink to 2 places after the decimal point)

Table E: Standardization of an EDTA Solution

Code of EDTA Solution: _____ Zinc Ion Molarity (Table B): = _____ M

Portion Volume of Zinc Solution = 10.00 mL = 0.01000 L

End-Point Indicator Volume Correction (Indicator Blank)

Final _____ mL - Start _____ mL = _____ mL

Titration Volumes (In Ink to 2 places after the decimal point)

	At Least Three Trials are Mandatory Additional Trials Only if Necessary					
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6
Final Volume (mL)						
Start Volume (mL)						
Titration Volume (mL)						
Indicator Blank Volume (mL)						
Blank Corrected Titration Volume (mL)						

Instructor's Initials on Completion of Titrations: _____ (10 points)

Mean Corrected Titration Volume of **Three** Acceptable Trials (Within a Range of **0.20 mL**) **Circle the Acceptable Trials**. State to 2 Places After the Decimal Point.

Mean Volume = _____ mL Range = _____ mL

Calculate the experimental molarity (**mol / L**) of the EDTA solution unknown. (5 points) State the value to 5 places after the decimal point. Show work.

Titration Volumes and Calculated Zinc Content

	At Least Three Tablet Titrations are Mandatory Additional Tablets Only if Necessary					
	Tablet 1	Tablet 2	Tablet 3	Tablet 4	Tablet 5	Tablet 6
Final Volume (mL)						
Start Volume (mL)						
Titration Volume (mL)						
Indicator Blank Volume (mL)						
Blank Corrected Titration Volume (mL)						
Calculated Experimental Zinc Content (mg) (to 2 places after the decimal)						

Instructor's Initials on Completion of Titrations: _____ (5 points)

3. Determination of Ca(II) and Mg(II) in a mixture.

Introduction

This method, called a complexometric titration, is used to find the total calcium and magnesium content of milk, sea water and various solid materials. It can also be used to determine the total hardness of fresh water provided the solutions used are diluted. The combined concentration of calcium and magnesium ions is considered to be the measure of water hardness.

The method uses a very large molecule called EDTA which forms a complex with calcium and magnesium ions. EDTA is short for ethylenediaminetetraacetic acid. A blue dye called Eriochrome Black T (ErioT) is used as the indicator. This blue dye also forms a complex with the calcium and magnesium ions, changing colour from blue to pink in the process. The dye–metal ion complex is less stable than the EDTA–metal ion complex. For the titration, the sample solution containing the calcium and magnesium ions is reacted with an excess of EDTA. The indicator is added and remains blue as all the Ca^{2+} and Mg^{2+} ions present arecomplexed with the EDTA.

A back titration is carried out using a solution of magnesium chloride. This forms a complex with the excess EDTA molecules until the end-point, when all the excess EDTA has been complexed. The remaining magnesium ions of the magnesium chloride solutionthen start to complex with ErioT indicator, immediately changing its colour from blue to pink.

The main reaction is

$Ca^{2+} + EDTA^{4-} \rightarrow [Ca\text{-}EDTA]^{2-}$

Back titration

$EDTA^{4-} + Mg^{2+} \rightarrow [Mg\text{-}EDTA]^{2-}$

Indicator reaction: note, ErioT is blue and ErioT-Mg is pink

$ErioT + Mg^{2+} \rightarrow ErioT\text{-}Mg$

Equipment Needed

- Burette
- 20 mL pipette
- 250 mL conical flasks
- 100 mL volumetric cylinder

Solutions Needed

EDTA: (ethylenediaminetetraaceticacid) 500 mL of a 0.05 molL-1 solution. Weigh 9.31 g of the EDTA salt and dissolve it in 500 mL of distilled water in a volumetric flask.

Buffer: Dissolve 7.0 g of ammonium chloride in 57 mL concentrated ammonia (see safety notes). Dilute to 100mL with distilled water in a volumetric flask. The pH should be 10.5.

$MgCl_2.6H_2O$: 0.025 molL-1 solution. Weigh 2.54 g of magnesium chloride hexahydrate and dilute to 500 mL with distilled water in a volumetric flask.

ErioT indicator: Dissolve 0.2 g of Eriochrome Black T indicator in 15 mL of concentrated ammonia solution (or 15 mL of triethanolamine) (see safety notes) and 5mL absolute ethanol. Do not store more than one to two days before use.

Method

Sample Preparation

For samples that are already in solution, such as freshwater, seawater and milk, no further preparation is needed.

For solid samples such as eggshells and limestone, the samples must first be dissolved in acid. Accurately weigh about 0.5 g of the solid into a small beaker or conical flask, add about 20 mL dilute hydrochloric acid and allow the solid to completely dissolve (this may take several minutes). Neutralise the unreacted acid with dilute sodium hydroxide solution until the pH of the solution is almost 7 (according to pH indicator paper). For eggshells, the inner membrane will remain undissolved and may be carefully removed from the solution. Transfer the solution to a 100 mL volumetric flask and make up to the mark with distilled water.

Standardisation of the EDTA Solution

1. Pipette a 10 mL sample of the EDTA solution into a conical flask.

2. Add 10 mL of ammonia buffer solution and 1 mL of Eriochrome Black T indicator solution.

3. Titrate the EDTA with the magnesium chloride solution until the endpoint is reached – a permanent colour change from blue to pink.

4. Having determined the average titre of the magnesium chloride solution, determine the number of moles used.

5. Given the Mg^{2+} : EDTA ratio of 1 : 1, calculate the concentration of your EDTA solution.

Titration Method for Seawater, Milk and Solid Samples

1. Pipette 10 mL of the sample solution into a conical flask.

2. Add 20 mL of 0.05 mol L−1 EDTA solution.

3. Add 10 mL of ammonia buffer, 50 mL of distilled water and 1 mL of Eriochrome Black T indicator solution.

4. Titrate the sample with the standard 0.025 molL−1 magnesium chloride solution until a permanent pink colour appears.

Titration Method for Fresh or Tap Water Samples

1. Add a 100 mL of the sample solution into a 250 mL conical flask.

2. Prepare a 0.005 mol L−1 EDTA solution by diluting the 0.05 mol L−1 EDTA solution by a factor of 1/10. Add 20mL of this diluted EDTA to the sample solution.

3. Add 10 mL of the ammonia buffer and 1 mL of Eriochrome Black T indicator solution.

4. Prepare a 0.0025 mol L−1 magnesium chloride solution by diluting the 0.025 mol L−1 magnesium chloride solution by a factor of 1/10.

5. Titrate the sample solution with this 0.0025 molL−1 magnesium chloride solution until a permanent pink colour appears. Repeat the titration with further samples until concordant results (titres agreeing within 0.1 mL) are obtained.

Figure 1 Colour changes for magnesium chloride back-titration in clear solution using Eriochrome Black T indicator. Left flask: blue colour well before endpoint (all Ca2+/Mg2+ ions complexed by excess EDTA, all indicator molecules uncomplexed). Centre flask: last trace of blue/purple colour just before endpoint (excess EDTA almost totally complexed by added Mg2+). Right flask: pink/red colour at endpoint (all EDTA complexed by added Mg2+, indicator also complexed).

Figure 2 Same colour changes for magnesium chloride back-titration as in Figure 1, but for cloudy (opaque) sample solution, eg milk. Left flask: blue colour well before endpoint. Centre flask: last trace of blue/purple. Right flask: pink/red colour at endpoint

Result Calculations

1. Calculate the total moles of EDTA added to the sample solution.

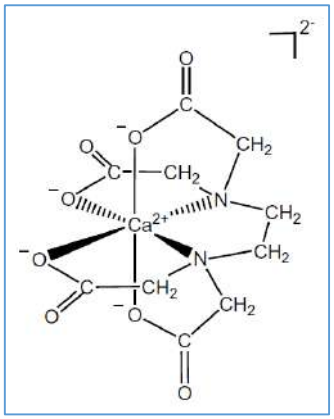
2. Calculate the moles of the magnesium chloride solution used in the back titration from your concordant results. From the equation of the titration below, the moles of Mg2+ will be equivalent to the moles of excess EDTA.

$$EDTA^{4-} + Mg^{2+} \rightarrow [Mg\text{-}EDTA]^{2-}$$

3. Given the ratio of Ca^{2+} + Mg^{2+} : EDTA = 1 : 1, calculate the moles of Ca^{2+} and Mg^{2+} that must have been complexed with EDTA by subtracting the excess EDTA from the total moles of EDTA added to the sample. This result is the moles of Ca^{2+} and Mg^{2+} in the sample solution.

Additional Notes

1. Ethylenediaminetetraacetic acid, EDTA is a large molecule which creates a complex with a metal ion, bonding through six coordination sites.



Complex formed by EDTA and calcium ions

2. The ammonia buffer (pH ~ 10.5) used here is needed as Eriochrome Black T only changes colour in the pH range 7 – 11.

3. The presence of some other metal ions eg copper, iron, cobalt, nickel, zinc, manganese − in high concentrations may introduce error to the determination of calcium and magnesium ions using this method, although this is unlikely.

4. As the concentration of Ca^{2+} and Mg^{2+} in the sample solution may vary considerably depending on the nature and source of the sample it may be necessary to vary the concentration of the EDTA(if the titre volume is too low) or to dilute your solutions (if the titre volume is too high). The average titre volume should be in the range of 10 – 30 mL.

Inorganic preparations:

1. Preparations of Potassium Trisoxalatoferrate(III) Trihydrate, $K_3[Fe(C_2O_4)_3].3H_2O$:

To prepare the complex trisoxalatoferrate(III), $Fe(C2O4)_3^{-3}$ anion and isolate it as its hydrated potassium salt, $K_3[Fe(C_2O_4)_3].3H_2O$. Also, to study the photochemical reduction of the sample.

THEORY:

Potassium trisoxalatoferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3].H_2O$ is a green crystalline salt, soluble in hot water but rather insoluble when cold. It can be prepared by the reaction of $K_2C_2O_4.H_2O$ with $FeCl_3.6H_2O$.

$3K_2C_2O_4.H_2O(aq) + FeCl_3.6H_2O(aq) \rightarrow K_3Fe(C_2O_4)_3].3H_2O(aq) + 3KCl(aq)$

Experimental:

A. Chemicals:

1. $K_2C_2O_4.H_2O$
2. $FeCl_3.6H_2O$
3. $K_3Fe(CN)_6$ solution

Apparatus:

1.Filterpaper
2.funnel
3. opaque objects

4. H_2SO_4 solution 4. Largebeaker

5.distilled water 5.test tubes

Procedure:

1. Weigh approximately 9.0 g of hydrated potassium oxalate, $K_2C_2O_4.H_2O$ into a 250 mL beaker.

2. Add 30 mL of distilled water and heat to dissolve (do not boil).

3. In a second small beaker dissolve 4.4 g of $FeCl_3.6H_2O$ in a minimum amount of cold water (10-15 mL). Add the $FeCl_3.6H_2O$ solution to the warm oxalate solution and stir with a glass rod. Allow the product to crystallize (away from strong sunlight) by cooling the solution in an ice-water mixture.

4. Collect the crystalline product by filtration. The product is $K_3Fe(C_2O_4)_3].3H_2O$.

NOTES

1. Heat must be applied as uniformly as possible.

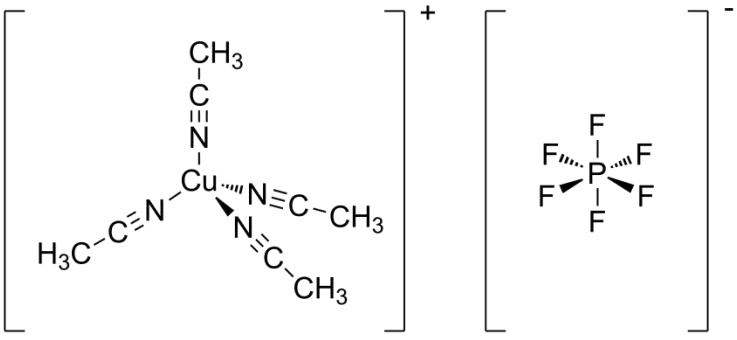
2. The addition of the mixture requires five to ten minutes.

3. The product is detached from the walls during cooling as it is difficult to remove when cold.

- Yield: …….… xxxxx g.
- Melting Point: ……yyyy……

2. Preparations of $[Cu(CH_3CN)_4]PF_6/ClO_4$

Tetrakis(acetonitrile)copper(I) hexafluorophosphate is a salt with the formula$[Cu(CH_3CN)_4]PF_6$. It is a colourless solid that is used in the synthesis of other copper complexes. The cation $[Cu(CH_3CN)_4]+$ is a well-known example of a transition metal nitrile complex.



As confirmed by X-ray crystallographic studies, copper(I) ion is coordinated to four almostlinear acetonitrile ligands in a nearly ideal tetrahedral geometry. Related complexes are known with other anions including the perchlorate, tetrafluoroborate, and nitrate. With the

weakly coordinating anion $B(C_6F_5)^{4-}$, salts of $[Cu(CH_3CN)_2]+$ are obtained. The acetonitrile ligands protect the Cu+ ion from oxidation to Cu^{2+}. Acetonitrile is not bound very strongly to the copper ion, thus the complex is a useful source of Cu(I). With other counteranions, complexes of $[Cu(MeCN)_3]^+$ are observed.

Synthesis:

$[Cu(CH_3CN)_4]PF6$ is generally produced by the addition of HPF_6 to a suspension of copper(I) oxide in acetonitrile.

$$Cu_2O + 2\ HPF_6 + 8\ CH_3CN \rightarrow 2\ [Cu(CH_3CN)_4]PF_6 + H_2O$$

The reaction is highly exothermic, and may bring the solution to a boil. Upon crystallization, the resulting microcrystals should be white, though a blue tinge is common, indicating the presence of Cu^{2+} impurities

Procedure:

Copper(II) sulphate pentahydrate (2.00 g,8.0 mmol, copper(II) nitrate can be used instead), sodium tetrafluoroborate (2.38 g, 21.6 mmol, other alkali tetrafluoroborate can be used instead), acetonitrile (2.68 g, 65.4mmol), copper wire coil (d ¼ 0.7 mm, 60 turns with d ¼ 6 mm, other metal copper source can be used instead) and distilled water (ca. 9 ml) were placed in a 16 ml plastic vial and tightlyclosed with a cap. This mixture was shaken several times and put in boiling water bath for 10 minutes. Then the vial wastaken out the bath and cooled to room temperature (RT) with water flow, shaken several times and put back into water bath for 10 minutes more. The operation (cooling – shaking – heating for 10 minutes) was repeated once or twice until blue color of Cu^{2+} disappeared. The resulting reaction mixture was cooled to RT, the copper wire was removed and the vial was again closed with the cap. The obtained white suspension in water was cooled in fridge to complete the precipitation of the product. It was then centrifuged, white solid was consistently washed and centrifuged twice with 5 ml of water (containing 0.1 g of acetonitrile), two times with 5 ml of ethyl acetate/ethanol 1 : 1 mixture (containing 0.2 g of acetonitrile) and twice with 5 ml of ethyl acetate (containing 0.1 g of acetonitrile). The obtained precipitate was dried at 50 ^{0}C in air for 2 hours and then in vacuum at RT to give 4.34 g of the product as white crystalline solid (yield 86%)

$[Cu(CH_3CN)_4][ClO_4]$. Copper(II) sulphate pentahydrate (2.00 g, 8.0 mmol), lithium perchlorate (2.30 g, 21.6 mmol, other alkali metal perchlorate can be used instead), acetonitrile (2.68 g, 65.4 mmol), distilled water (ca.9 ml) were used as starting reagents. The product has been obtained as white crystalline solid, 4.29 g of (yield 82%).

Conclusions

In conclusion, we elaborated an efficient protocol for the synthesis of $[Cu(CH_3CN)_4]X$ complexes (X =BF_4^-, PF_6^-, ClO_4^-)using stable, inexpensive and low toxic materials. The protocolmakes possible to carry out the reaction in aqueous media andminimizes the amount of toxic acetonitrile in the synthesis.According to this protocol the targeted complexes could beobtained in high yield (82–87%) as pure crystalline material.

3. Synthesis of tris(ethylenediamine) nickel(II) chloride

The equation for the synthetic reaction you will carry out is:

$NiCl_2 \cdot 6H_2O$ (aq) + 3 $C_2H_8N_2$ (aq) → $[Ni(C_2H_8N_2)_3]Cl_2$ (s) + $6H_2O$ ……(l)

The procedure for making [Ni(C2H8N2)3]Cl2 (tris(ethylenediamine)nickel(II) chloride) is given below. It will be up to each group to determine what measurements and calculations must be made to determine the limiting reagent, the theoretical yield and percent yield of the solid product, and, in the written report, to account for the difference between theoretical and percent yield (lost product, unreacted starting material, etc.). Note that the ethylenediamine is provided as an aqueous solution ($C_2H_8N_2$ (aq)), not as a pure compound. You must take this into account in your limiting reactant calculations.

Safety: In this part of the experiment you will be using acetone, which is flammable, so there will be no flames in the lab during this experiment. Ethylenediamine is very corrosive, and it will be stored in the fume hood to reduce the hazard of any spills. You should wear gloves when handling this solution, since it is corrosive.

Make sure all glassware is very clean -- any residue of sodium acetate from Part A will interfere with this reaction.

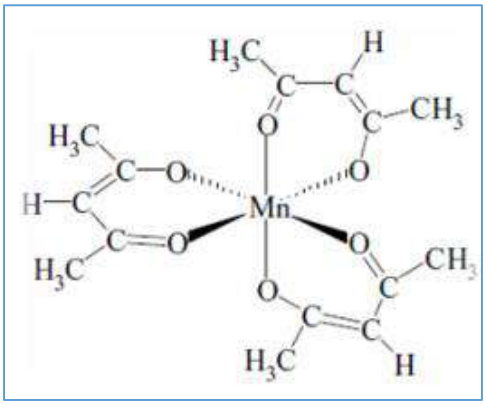
(Use the quantities and procedure shown below, or follow the instructions included in the published protocols, if desired.)

Measure about 2 to 2.5 grams of nickel(II) chloride hexahydrate, and put it in a 150-mL beaker. Dissolve it in as little DI water as possible (5 mL maximum). Use a glass-stirring rod to mix the solution. Slowly add 10.00 mL (carefully measured) of 25.0% (m/m; mass percent) ethylenediamine-water solution (density of the solution is 0.950 g/mL), again using the stirring rod to mix. Add about 25 mL of acetone (extremely flammable) to the reaction mixture, in 5 increments of about 5 mL each (thoroughly mix after each 5-mL addition). Continue stirring until precipitation begins.

Cool the beaker on ice for about 10-15 minutes to maximize precipitation (if the beaker is warm to the touch after the addition of acetone, wait for it to cool to near room temperature before putting it in the ice bath

4. Preparation of tris(acetylacetonate)manganese(III)

Dissolve 0.6 g of manganese(II) chloride and 1.6 g of $NaOAc \cdot 3H_2O$ in 25 cm3 of water. Add 3 cm3 of acetylacetone slowly with stirring. Treat the resultant two-phase system with potassium permangante solution (1.2 g in 6 cm3 of water) and after a few minutes add, in small amounts with stirring, sodium acetate solution (1.6 g $NaOAc \cdot 3H_2O$ in 6 cm3 water). Heat the solution to about 60°? C for 10 minutes, cool in ice-cold water and filter at the pump. Wash the product with ice-cold water and small quantities of acetone to facilitate drying. Dry at the pump and determine the yield.



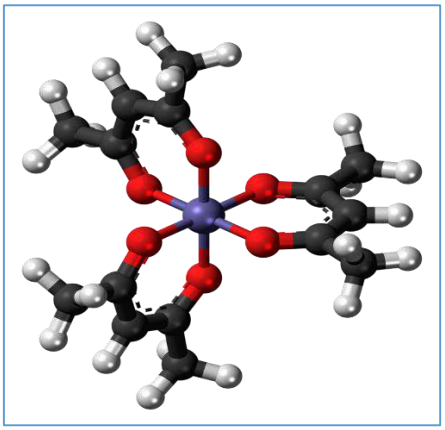
Structure of tris(acetylacetonate)manganese(III)

5. Preparation of tris(acetylacetonate)iron(III)

Dissolve 5 g of ferric sulfate in 25 cm3 of water and add 4 cm3 of 2,4 pentanedione. Dissolve 3.5 g of sodium acetate in 25 cm3 of water. Slowly add the second solution to the first, stirring continuously. Filter off the red crystals and air dry them. Weigh the dried product.

$Fe(acac)_3$ is prepared by treating freshly precipitated $Fe(OH)_3$ with acetylacetone.

$$Fe(OH)_3 + 3\ HC_5H_7O_2 \rightarrow Fe(C_5H_7O_2)_3 + 3\ H_2O$$



Structure of tris(acetylacetonate)iron(III)

5. Synthesis of C*is* and *trans* potassium-dioxalato diaquo chromate (III) $K[Cr(C_2O_4)_2(H_2O)2].2H_2O$

Objective

To prepare *cis* and *trans* potassium-dioxalato diaquo chromate complex.

Requirements

Chemicals: Oxalic acid crystal 3 g

$K_2Cr_2O_7$ 1 g

C_2H_5OH 20 mL

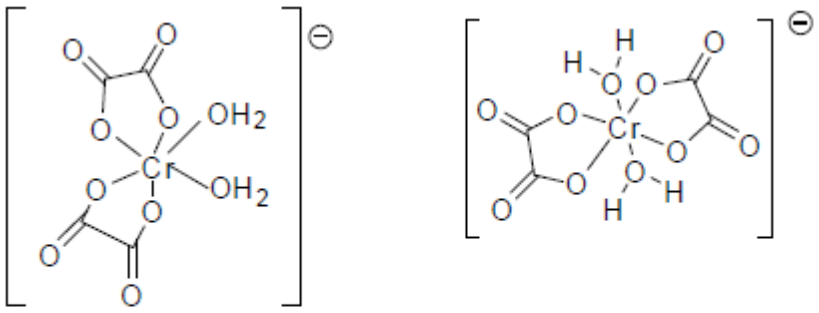
Apparatus: Electronic weighing machine, beaker 500 mL, beaker 250 mL, Bunsen burner, desiccator, filtration apparatus, conical flask, Funnel, Glass rod, Pair of tongs, Tripod stand, Watch glass, Water bath, Wire guaze.

Theory

Cis and *trans* potassium dioxalato diaquo chromate (III) ionize in the following fashion:

$$K[Cr(C_2O_4)_2(H_2O)_2].2H_2O \longrightarrow K^+ + [Cr(C_2O_4)_2(H_2O)_2]^- + 2H_2O$$

The complex ion obtained from above ionization process exists in the *cis* and *trans* geometrical isomeric forms which can be represented as:

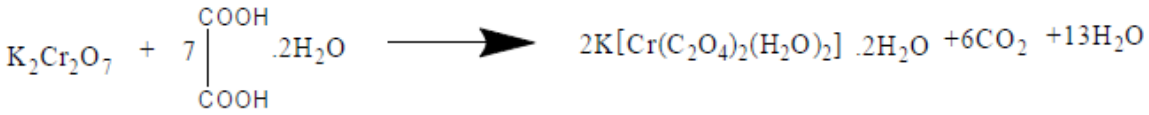


Cis isomer Trans isomer

Structure of *cis* and *trans* dioxalato diaquo chromate complex ions

A. *Cis* potassium dioxalato diaquo chromate (III) complex K [Cr(C2O4)2(H2O)2]2H2O

This isomer is prepared by the reaction of K2Cr2O7 according to the following reaction:



B. *Trans* potassium dioxalato diaquo chromate (III) complex K[Cr(C2O4)2(H2O)2].2H2O

This isomer is prepared by the reaction of K2Cr2O7 according to the following reaction.

Procedure

A. *Cis* potassium dioxalato diaquo chromate (III) complex

Preparation of the *cis* isomer involves the following steps:

Step I At first, 3g of oxalic acid and 1g of K2Cr2O7 are mixed with each other and grinded to obtain the powder form.

Step II Take this mixture in the china dish and heat the content in china dish gently on a low flame by which a vigorous reaction will occur with the evolution of CO2 and water vapour. Finally the mixture will become deep colored liquid.

Step III Now without cooling the liquid, 20 mL C2H5OH is added over this liquid and triturate the content by metallic spatula until the solid mass is formed.

Step IV Now warm the content until the product cannot be obtained in the form of granular crystals. The crystals of *cis* potassium dioxalato diaquo (III) complex look black in the diffused day light which are finally weigh.

B. *Trans* potassium dioxalato diaquo chromate (III) complex

Preparation of the *trans* isomer involve the following steps:

Step I Take 3g of oxalic acid crystal in a beaker and add small amount of water and heat to dissolve the oxalic acid crystal in water.

Step II Take 1g of K2Cr2O7 and small amount of water in a boiling tube and heat to dissolve the K2Cr2O7 in water.

Step III Now introduce the content of boiling tube in the beaker containing oxalic acid solution and cover the beaker by watch glass.

Step IV Now cool the dark coloured content of beaker and transfer it to a china dish. The content of china dish is kept in air for 36-48 hours by which volume is reduced to one third of the original volume.

Step V Now the crystals of *trans* isomer get deposited and filter by regular filter paper with the help of funnel which are washed by water and ethyl alcohol and finally weigh the crystals of trans isomer.

Result

A. The yield of *cis* potassium dioxalato diaquo chromate (III) complex is ……..g.

B. The yield of *trans* potassium dioxalato diaquo chromate (III) complex is …….g.

6. Preparation of Tetraamminecarbonatocobalt (III) ion

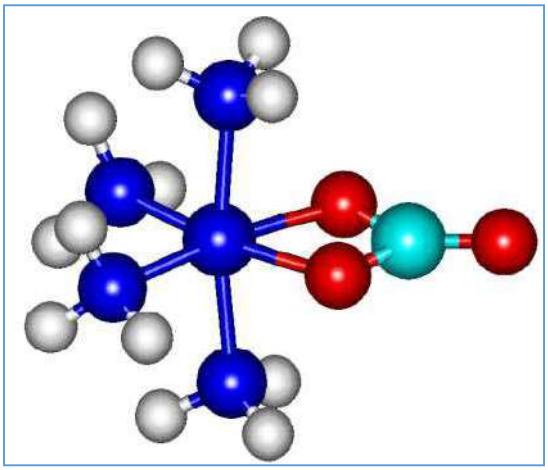
Experiments involving the aqueous preparation of cobalt(III) complexes have been a familiar feature in many textbooks written for use in the inorganic chemistry laboratory. Coordination compounds of Co(III) have been of particular interest because their complexes, kinetically inert, undergo ligand exchange very slowly compared with various other transition metals.

The synthesis of [Co(NH3)4CO3]NO3 involves the following *unbalanced* equation.

Co(NO3)2 + NH3(aq) + (NH4)2CO3 + H2O2 → [Co(NH3)4CO3]NO3 + NH4NO3 + H2O

Cobalt nitrate [Co(NO3)2] is deliquescent (tends to absorb atmospheric water vapor). Upon exposure to atmospheric moisture, cobalt nitrate has the formula Co(NO3)2▪6H2O. Co(II) complexes react very rapidly by ligand exchange, thus a possible first step in the reaction:

$$Co(OH_2)_6^{2+} + 4NH_3(aq) + CO_3^{2-} \rightarrow Co(NH_3)_4CO_3 + 6H_2O$$



The intermediate tetraamminecarbonatocobalt(II) could then be oxidized by addition of H2O2 to form [Co(NH3)4CO3]+. Compounds with a carbonato ligand are useful intermediates in the synthesis of coordination complexes. The carbonate ion is easily removed by the additional of HCl and the carbonate forms carbon dioxide. The carbonate ion is a bidentate ligand and leaves two open coordination sites. Water molecules or chloride ions may occupy the open coordination sites. Water is not a particularly strong

ligand and addition of ions such as X^-, NH_3, or NO_2^- leads to the replacement of these coordinated water molecules.

Ammonium carbonate, used as a smelling salt, is an irritant to the mucous membranes and reactions should be kept in a fume hood as much as possible. Before weighing, open the bottle in the hood to remove ammonia vapor from the bottle. The powder tends to clump together and it may be necessary to break apart the $(NH_4)_2CO_3$ using a rubber mallet/plastic bag and/or grind using a glass mortar and pestle prior to weighing. Cobalt nitrate hexahydrate is hygroscopic and will absorb atmospheric moisture. Use a top loading balance for the synthesis and an analytical balance for the characterization step. Dissolve 0.208 *mol* of $(NH_4)_2CO_3$ in 60 mL of H2O in a beaker under constant stirring. Add 60 mL of concentrated aqueous NH3 (ammonium hydroxide). Pour this solution, while stirring, into a solution containing 0.0515 *mol* of $[Co(OH_2)_6](NO_3)_2$ in 30 mL of H_2O. *Slowly* add 8 mL of a 30% H_2O_2 solution dropwise (***Warning: H2O2 is a strong oxidizing agent that can cause severe burns. Use proper gloves while handling. If a spill occurs, wash the affected areas immediately with water.***). Concentrate to about 90-100 mL using a hot plate. The use of an evaporating dish may be used in place of a beaker to facilitate evaporation. Maintain the temperature of the solution near 85°C and do not allow the solution to boil. Add 5 g of $(NH_4)_2CO_3$, in small portions, during the course of the evaporation. Suction filter the hot solution if there are any undissolved materials. Cool to about 5°C in an ice water bath and then isolate the red crystalline product by

suction filtration into a clean side-arm Erlenmeyer flask. Transfer the filtrate to a separate 250 mL Erlenmeyer flask and retain. Wash the product with a small amount of ice-cold water and then with a small amount of 95% ethanol. Allow the product to dry, place on a watch glass, dry in a drying oven at 100 °C (if available). Place the product in a weighed sample bag, weigh the product and sample bag, and determine the percent yield. If needed, further reduce the volume of the retained filtrate and perform a second evaporation using the evaporating dish and second filtration. On the same day, time permitting, collect an IR spectrum of the product using the Perkin Elmer Spectrum 1 Infrared Spectrometer (FT-IR). Ensure the peaks are labeled. Prepare a solution, using a 25 mL volumetric flask, with a concentration near 0.005 M. Collect the UV-Vis spectra in a cuvette from 285 nm to 700 nm. The absorbance should be between 0.5 and 1.0. Record the wavelength of maximum absorption and absorbance.

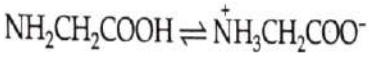
Adjust the concentration and prepare a second solution if the absorbance is outside that range. Measure, using a Hanna Instruments HI9093 conductivity meter, the conductance of tap water, deionized water, the solution of [Co(NH3)4CO3]NO3, and solutions of KCl, MgCl2, and FeCl3 (data for the latter 3 may be shared) near the same concentration as the cobalt compound. Calculate the molar conductivity for each compound.

The IR, UV-Vis spectra, and conductivity data may be collected before, during, or after the synthesis of [Co(NH3)5Cl]Cl2. Utilize your time wisely. One person in the class needs to collect the IR and UV-visible data for [Co(OH2)6](NO3)2 and NaNO3. Retain, for the next experiment, the product in a weighed and labeled (initial and last name, complete formula compound, and date) sample bag. Discard the filtrate wash solution in the appropriate “metal waste” containers in the fume hood. Do not tightly cap the waste bottle, for safety reasons, because of the decomposition of carbonates and pressure increase inside a closed container. Retain the product for the next part of the experiment.

C10P: Organic Chemistry Lab

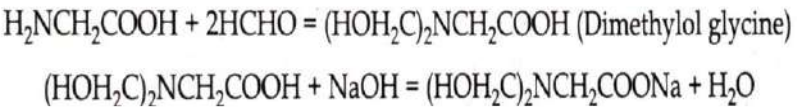
1. Estimation of Glycine (Sorensen's Formol Method)

In an aqueous solution of glycine the following equilibrium exists:



$$NH_2CH_2COOH \rightleftharpoons \overset{+}{N}H_3CH_2COO^-$$

The zwitterionic structure of glycine is responsible for the inability of this amino acid to be titrated directly against alkali. However, protection of the amino group with formalin enables glycine to behave as a monobasic acid and titration against a standard alkali solution becomes possible.



$$H_2NCH_2COOH + 2HCHO = (HOH_2C)_2NCH_2COOH \text{ (Dimethylol glycine)}$$

$$(HOH_2C)_2NCH_2COOH + NaOH = (HOH_2C)_2NCH_2COONa + H_2O$$

Thus 1000 mL of (N) NaOH≡ 1g equivalent of glycine = 75 g of glycine

Chemicals required:

1. Standard (N/20) oxalic acid solution: Weigh out accurately~ 0.8 g (w) (exactly 0.7879 g) of A.R oxalic acid, dissolve it in distilled water in a 250 mL volumetric flask and make up the volume with distilled water up to the mark. Mix well to ensure homogeneity of the solution.

2. **(N/20) NaOH solution:** Dissolve ~1 g of solid NaOH in 500 mL of distilled water.

3. **Formalin solution:** 37% v/v.

4. **Phenolphthalein indicator:** 0.5% in (1:1) ethanol.

5. **(N/20) Glycine solution:** Dissolve 0.9-1.0 g of glycine in 250 mL of distilled water.

Procedure:

1. **Standardization of NaOH against Standard oxalic acid solution**: Pipette out 25 mL of standard oxalic acid solution in a 250 mL conical flask. Add 2-3 drops f phenolphthalein indicator. Add NaOH solution from a burette until the appearance of a faint pink colour.

2. Neutralization of formalin solution: Take 10 ml of formalin solution in a beaker, 25 mL of distilled water to it. Then add 1-2 drops phenolphthalein indicator to the solution. Add (N/20) NaOH solution dropwise till the appearance of a very faint pink color.

3. Estimation of glycine: Pipette out 25 ml of glycine solution in a 250 mL conical flask. 25 mL of the neutralized formalin solution and 2 drops of phenolphthalein indicator to it. Titrate against standard sodium hydroxide solution till the appearance of light pink color.

Results:

1. Standardization of sodium hydroxide solution against standard oxalic acid

Volume of oxalic acid (mL)	**Volume of NaOH (mL)**	**Mean volume of NaOH (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of oxalic acid solution = (w/0.7879) (N/20)

So the strength of NaOH solution (S_1) = (25 x w) / (V_1 x 0.7879) (N/20)

2. Estimation of Glycine:

Volume of Glycine (mL)	**Volume of of neutralized formalin solution (mL)**	**Volume of NaOH (mL)**	**Mean volume of NaOH (mL) (V_2)**
25	25	x	
25	25	y	(x + y+ z)/3
25	25	z	

Calculation:

1000 mL of (N) NaOH ≡ 1000 mL of (N) glycine ≡ 75 g of glycine

So V_2 mL of S_1(N) NaOH ≡ $(75 \times V_2 \times S_1)/1000$ g of glycine

25 mL of glycine solution contains $(75 \times V_2 \times S_1)/1000$ g of glycine

So 1000 mL of glycine solution contains

$(40 \times 75 \times V_2 \times S_1)/1000$ g of glycine

$= (40 \times 75 \times V_2 \times 25w/V_1 \times 0.7879 \times 20)/1000$ g of glycine

$= 4.7595 \times (wV_2/V_1)$ g of glycine.

2. Estimation of Glucose (using Fehling's Solution)

Principle: Glucose a reducing sugar, is quantitively oxidized by Fehling solutions under boiling conditions to gluconate along with precipitation of red cuprous oxide. Fehling's solution is a mixture of an aq. solution of sodium potassium tartrate (also known as Rochelle salt) in alkali (Fehling II or B) and a solution of $CuSO_4$ containing a little acid (Fehling I or A) in equal volume.

Chemical required:

1. Standard glucose solution: Weigh out accurately~ 0.5 g of (A.R) glucose in a 100 mL volumetric flask. Dissolve it in distilled water and make up to the mark with distilled water and mix uniformly.

2. Fehling's solution A: Dissolve 17.32 g of copper sulfate pentahydrate in distilled water, add 1 drop dil. sulfuric acid (to prevent hydrolysis of cu-sulfate) and dilute to 250 mL and mix uniformly.

3. Fehling solution B: Dissolve 86.5 g of sodium potassium tartrate and 25 g of sodium hydroxide in distilled water. Dilute to 250 mL with distilled water and mix uniformly.

4. Unknown glucose solution: Weigh out accurately ~ 0.4-0.5 g of (A.R) glucose for 100 mL solution in a volumetric flask. Dissolve it in distilled water and make up to the mark with distilled water and mix uniformly.

Procedure:

1. Standardization of Fehling's solution: Pipette out 10 mL of Fehling's solution A and 10 mL of Fehling's solution B in a 250 mL conical flask. Boil the mixture gently on an asbestos centered wire gauge. Add standard glucose solution from a burette to the boiling Fehling's solution till the supernatant liquid becomes colorless with the precipitation of bright brick red cuprous oxide. The solution should be kept boiling uniformly throughout the titration.

2. Estimation of unknown glucose solution: Use unknown glucose solution instead of the known glucose solution and repeat the procedure as described under the heading of "'standardization of Fehling's solution".

Results:

1. Standardization of Fehling's solution:

Volume of Fehling's solution (mL)	Volume of Known glucose solution (mL)	Mean volume of Known glucose solution (mL) (V_1)
10+10	a	
10+10	b	$(a+b+c)/3$
10+10	c	

2. Estimation of unknown glucose solution:

Volume of Fehling's solution (mL)	Volume of unknown glucose solution (mL)	Mean volume of unknown glucose solution (mL) (V_2)
10+10	x	
10+10	y	$(x+y+z)/3$
10+10	z	

Calculation:

Let the weight of glucose taken for the preparation of standard glucose solution is w g.

If V_1 mL of standard glucose solution and V_2 mL of invert sugar solution are needed for the titration of 20 mL of Fehling's solution then

Weight of glucose in V_1 mL of standard glucose solution=the weight of glucose in V_2 mL of unknown glucose solution.

Now 100 mL of standard glucose solution contains w g of glucose

So V_1 mL of standard glucose solution contains $[(w \times V_1)/100]$ g of glucose

Hence V_2 mL of unknown glucose solution contains $[(w \times V_1)/100]$ g of glucose

Thus 100 mL of unknown glucose solution contains $[(w \times V_1)/V_2]$g of glucose

So the strength of unknown glucose solution is $[(w \times V_1)/V_2]\%$.

3. Estimation of Sucrose (using Fehling's Solution)

Principle: Sucrose is a non-reducing sugar. So, it does not react with Fehling's solution. Acid hydrolysis (dilute HCl) of sucrose yields glucose and fructose (invert sugar). Both glucose and fructose can be quantitatively oxidized by Fehling's solution to form a bright brick red precipitate of cuprous oxide.

Chemical required:

1. Standard glucose solution: Weigh out accurately~ 0.5 g of (A.R) glucose in a 100 mL volumetric flask. Dissolve it in distilled water and make up to the mark with distilled water and mix uniformly.

2. Fehling's solution A: Dissolve 17.32 g of copper sulfate pentahydrate in distilled water; add 1 drop of dil. sulfuric acid and dilute to 250 mL and mix uniformly.

3. Fehling solution B: Dissolve 86.5 g of sodium potassium tartarate and 25 g of sodium hydroxide in distilled water. Dilute to 250 mL with distilled water and mix uniformly.

4. Unknown sucrose solution: Weigh out accurately ~ 2 g of (A.R) sucrose in a 100 mL volumetric flask. Dissolve it in distilled water and make up to the mark with distilled water and mix uniformly.

Procedure:

1. standardization of Fehling's solution: Pipette out 10 mL of Fehling's solution A and 10 mL of Fehling's solution B in a 250 mL conical flask. Boil the mixture gently on an asbestos centered wire gauge. Add standard glucose solution from a burette to the boiling Fehling's solution till the supernatant liquid becomes colorless with the precipitation of bright brick red cuprous oxide.

2. Estimation of unknown sucrose solution:

a. Hydrolysis of sucrose: Pipette out 25 mL of unknown sucrose solution in a 250 mL conical flask. Add 25 mL of distilled water and 2-3 mL of cone. HO. Heat the-solution on a boiling water bath for 15 minutes. Cool the solution to room temperature and carefully neutralize with powdered sodium carbonate avoiding excess. Transfer the solution quantitatively into a 100 mL volumetric flask and make up to the mark with distilled water. Shake the solution to ensure uniform mixing.

b. Estimation of inyert sugar: Pipette out 10 mL of Fehling's solution A and 10 mL of Fehling's solution B in a 250 mL conical flask. Boil the mixture gently on an asbestos centred wire gauge. Add hydrolysed sucrose (invert sugar) solution from a burette to the boiling Fehling's solution till the supernatant liquid becomes colorless with the precipitation of bright brick red cuprous oxide.

Results:

1. standardization of Fehling's solution:

Volume of Fehling's solution (mL)	Volume of Known glucose solution (mL)	Mean volume of Known glucose solution (mL) (V_1)
10+10	a	
10+10	b	$(a+b+c)/3$
10+10	c	

2. Estimation of unknown sucrose solution:

Volume of Fehling's solution (mL)	Volume of invert sugar solution (mL)	Mean volume of unknown invert sugar solution (mL) (V_2)
10+10	x	
10+10	y	$(x+y+z)/3$
10+10	z	

Calculation:

Let the weight of glucose taken for the preparation of standard glucose solution is w g.

If V_1 mL of standard glucose solution and V_2 mL of invert sugar solution are needed for the titration of 20 mL of Fehling's solution then

Weight of glucose in V_1 mL of standard glucose solution=the weight of glucose in V_2 mL of unknown glucose solution.

Now 100 mL of standard glucose solution contains w g of glucose

So V_1 mL of standard glucose solution contains $[(w \times V_1)/100]$ g of glucose

Hence V_2 mL of invert sugar solution $\equiv [(w \times V_1)/100]$ g of glucose

Thus 100 mL of invert sugar solution $\equiv [(w \times V_1)/V_2]$g of glucose

Now 360 g of glucose $\equiv$ 342 g of sucrose

So $[(w \times V_1)/V_2]$g of glucose $\equiv [342 \times (w \times V_1)/360 \times V_2]$g of sucrose $= 0.95 \times [(w \times V_1)/V_2]$g of sucrose

Thus 25 mL of sucrose solution contains $0.95 \times [(w \times V_1)/V_2]$g of sucrose

So the strength of unknown sucrose solution is $[0.95 \times 4 \times (w \times V_1)/V_2]\%$.

4. Estimation of Vitamin C

Principle: Vitamin C (ascorbic acid) is quantitatively oxidized by iodine to dehydroascorbic acid. A known volume of an aqueous solution of vitamin C is treated with a measured excess of standard iodine solution and the excess iodine is back titrated against a standard solution of sodium thiosulfate. Iodine consumed by vitamin C is thus estimated.

$$I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

100 mL of (N) thiosulfate ≡1000 mL of (N) iodine ≡ 1000 mL of (N) vitamin C [equivalent weight of vitamin C ≡ 88.06 g]

Chemical required:

1. Standard (N/20) $K_2Cr_2O_7$ solution: Weigh out accurately ~ 0.6129 g (w) of (A.R) $K_2Cr_2O_7$ in 250 mL volumetric flask, dissolve in distilled water and make up to the mark with distilled water. Mix the solution uniformly.

2. (N/20) I_2 solution: Mix ~ 1.6 g of solid iodine and 2 g of potassium iodide. Add 10-15 rnL of water and stir to dissolve. Dilute the solution to 250 mL with distilled water.

3. (N/20) sodium thiosulfate solution: Dissolve 3-4 g of sodium thiosulfate pentahydrate in distilled water dilute to 250 mL and mix uniformly.

4. 10% potassium iodide solution.

5. 1% Starch Indicator.

6. Sample vitamin C solution: Dissolve ~ 1-1.2 g of vitamin C in distilled water, dilute to 250 mL and mix uniformly.

Procedure:

1. Standardization of sodium thiosulfate solution against standard potassium dichromate solution: Pipette out 25 ml of standard (N/ 20) $K_2Cr_2O_7$ solution in a 500 mL conical flask Add 25 mL of 4(N) sulfuric acid and 10 mL of 10% Kl (or 1 g of solid KI) solution to it. Cover the

flask with a small watch glass and allow to stand in dark for 4-5 minutes. Dilute with 150 mL of distilled water to adjust the acidity to ~ 0.5(N). Titrate with sodium thiosulfate solution till the appearance of a straw yellow color. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the blue color disappears with the appearance of a light green color.

2. Standardization of iodine solution against standard sodium thiosulfate solution: Pipette out 25 mL of iodine solution in a 500 mL conical flask. Add 75 mL of distilled water to it. Titrate with standard sodium thiosulfate solution till the appearance of a straw yellow color. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue color. (end point: colourless)

3. Estimation of vitamin C solution: Pipette out 25 mL of the unknown vitamin C solution in a 500 mL conical flask. Add 25 mL of distilled water to it. Then add 1 mL of 4(N) sulfuric acid to adjust the acidity to ~ 0.l(N). Add a measured excess (25 x x mL) of standard iodine solution so that the color of iodine persists in solution. Allow to stand for ~ 1 minute. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Titrate against standard sodium thiosulfate solution till the disappearance of the blue colour. (End point: colourless).

Results:

1. Standardisation of sodium thiosulfate solution against standard potassium dichromate solution:

Volume of $K_2Cr_2O_7$ (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of $K_2Cr_2O_7$ solution = (w/0.6129) (N/20)

So the strength of $Na_2S_2O_3$ solution = (25 x w) / (V_1 x 0.6129) (N/20)

2. Standardisation of iodine solution against standard sodium thiosulfate solution:

Volume of I_2 (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_2)**
25	x	
25	y	(x + y+ z)/3
25	z	

3. Estimation of vitamin C solution:

Volume of vitamin C solution (mL)	Volume of I_2 solution (mL)	Volume of $Na_2S_2O_3$ (mL)	Mean volume of $Na_2S_2O_3$ (mL) (V_3)
25	25 × x	d	
25	25 × y	e	(d + e+ f)/3
25	25 × z	f	

Calculation:

25 mL of iodine solution ≡ V_2 mL of S_1(N) sodium thiosulfate solution

So (25 × x) mL of iodine solution ≡ (V_2 × x) mL of S_1(N) sodium thiosulfate solution

Thus iodine consumed by vitamin C≡ (xV_2 – V_3) mL of S_1(N) sodium thiosulfate solution

Now 1000 mL of (N) thiosulfate ≡ 1000 mL of (N) iodine ≡ 1000 mL of (N) vitamin C ≡ 88.06 g of vitamin C [equivalent weight of vitamin C = 88.06]

So (xV_2–V_3) mL of S_1(N) sodium thiosulfate ≡ [88.06 × (xV_2–V_3)S_1]/1000 g of vitamin C

= [88.06 × (xV_2–V_3)25 × w]/(1000 × V_1 × 0.6129 × 20)g of vitamin C

Thus 25 mL of vitamin C solution contains

= [88.06 × (xV_2–V_3)25 × w]/(1000 × V_1 × 0.6129 × 20)g of vitamin C

Hence 1000 mL of vitamin C solution contains

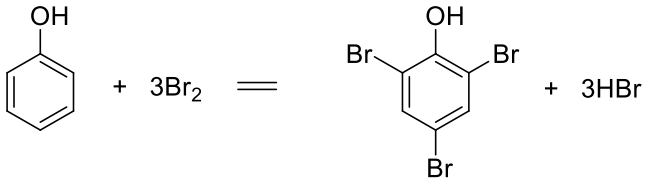
= [88.06 × (xV_2–V_3) × 1000 × w]/(1000 × V_1 × 0.6129 × 20)g of vitamin C

= [88.06 × (xV_2–V_3) × w]/(V_1 × 0.6129 × 20)g of vitamin C

= 7.1839 × (xV_2–V_3) × w]/(V_1) g of vitamin C.

5. Estimation of phenol by bromination (Bromate-Bromide) method

Principle: Phenol reacts quantitatively with bromine to form a white precipitate of 2,4,6 tribromophenol.



Thus 6000 mL (N) bromine ≡94·g of phenol

So 1000 mL of (N) bromine ≡ (94/6) g i.e. 15.67 g of phenol

Hence the equivalent weight of phenol is 15.67

The phenol solution is treated with measured excess of ($KBr+KBrO_3$) solution which is equivalent to bromine in acidic medium. The excess bromine is allowed to react with sufficient potassium iodide. Bromine oxidizes iodide to iodine. This iodine is estimated by titration against a standard solution of sodium thiosulfate. Thus, the amount of bromine left after consumption by phenol is determined. Difference between added and remaining bromine corresponds to the amount of phenol in the volume of sample solution taken for titration.

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 6KCl + 3H_2O$$
$$Br_2 + 2KI = 2KBr + I_2$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

100 mL of (N) thiosulfate ≡1000 mL of (N) iodine ≡ 1000 mL of (N) Br_2 ≡ 1000 mL of (N) phenol≡15.67 g of phenol.

In acid medium bromate reacts according to the following equation

$$BrO_3^- + 6H^+ + 6e = Br^- + 3H_2O$$

So the equivalent weight of $KBrO_3$ = (molecular weight of $KBrO_3$/ 6) = (167/6) = 27.8334.

Chemicals required:

1. Standard (N/20) $KBrO_3$-KBr solution: Weigh out accurately ~ 0.35 g (w) (exactly 0.3479 g) of (A.R) **$KBrO_3$** and ~5 g of KBr in a 250 mL volumetric flask. Dissolve in distilled water and make up to the mark with distilled water.

2. Sodium thiosulfate solution: Dissolve·3-4 g of sodium thiosulfate pentahydrate in distilled water and dilute to 250 mL with distilled water.

3. 10% Potassium iodide solution

4. 1% Starch solution

5. Sample phenol solution: Dissolve 3-4 g of pure phenol in distilled water and dilute to one liter with distilled water. Dilute 20-25 mL of this stock solution to 100 mL with distilled water in a 100 mL volumetric flask. 25 mL of this diluted solution may be used for titration.

Procedure:

1. Standardisation of sodium thiosulfate solution against standard $KBrO_3$-KBr solution: Pipette out 25 mL of standard $KBrO_3$-KBr solution in a 500 mL conical flask. Add 10 mL of 10% potassium iodide solution or 1 g of solid potassium iodide to this solution. Then add 5 mL conc. HCl to adjust the acidity to ~ 1.5(N). Cover the flask with a small watch glass and keep

in dark for 3-4 minutes. Dilute with 100 mL of water to adjust the acidity of the resulting solution to ~ 0.5(N). Titrate the liberated iodine with sodium thiosulfate solution till the appearance of a straw yellow colour. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue colour. (end point: colourless)

2. Estimation of phenol: Transfer the sample phenol solution into a volumetric flask of definite size as directed and make up to the mark with distilled water.

Pipette out 25 mL of diluted phenol solution in a 500 mL conical flask. Add 10-12 mL of cone. HCl to maintain the acidity at ~ 3(N). Add a measured excess (25 x *x*) mL of standard $KBrO_3$-KBr solution so that a permanent yellow colour due to an excess of free bromine persists. Cover the flask with a small watch glass, shake well and allow to stand at room temperature in the dark for 5 minutes with occasional shaking. Add 10 mL of 10% potassium iodide solution or 1 gm of solid potassium iodide. Dilute with 150 mL of distilled water adjust the acidity ~ 0.5(N). Titrate the liberate iodine with sodium thiosulfate solution till the appearance of a straw yellow colour. Add 2 mL of 1% starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue colour leaving white precipitate of 2,4,6 tribromophenol in the solution.

1. Standardisation of sodium thiosulfate solution against standard $KBrO_3$-KBr solution:

Volume of $K_2Cr_2O_7$ (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of $KBrO_3$-KBr solution = (w/0.3479) (N/20)

So, the strength of sodium thiosulfate = S_1 = (25x w) / (V_1 x 0.3479) (N/20)

2. Estimation of phenol:

Volume of phenol solution (mL)	**Volume of KBrO3-KBr solution (mL)**	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_3)**
25	25 × x	x	
25	25 × y	y	(x + y+ z)/3
25	25 × z	z	

Calculation:

25 mL of $KBrO_3$-KBr solution ≡ V_1 mL of S_1 (N) sodium thiosulfate solution

So (25×x) mL of $KBrO_3$-KBr solution ≡ (V_1× x) mL of S_1 (N) sodium thiosulfate solution

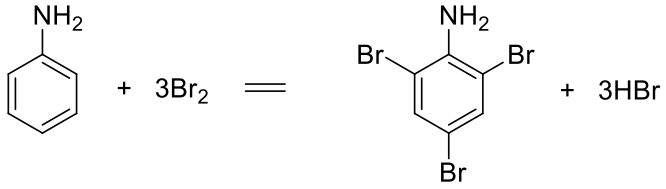
Bromine left after consumption by phenol ≡ V_2 mL of S_1 (N) sodium thiosulfate solution

Hence bromine consumed by phenol ≡ ($x$$V_1$-$V_2$) mL of S_1 (N) sodium thiosulfate solution

Now 1000 mL of (N) $Na_2S_2O_3$ ≡ 15.67 g of phenol
So (xV_1-V_2) mL S_1(N) $Na_2S_2O_3$ ≡ $[15.67 \times (xV_1-V_2) \times S_1]/1000$ g of phenol
25 mL of phenol solution contains $[15.67 \times (xV_1-V_2) \times S_1]/1000$ g of phenol
So 1000 mL of phenol solution contains $[15.67 \times (xV_1-V_2) \times S_1]/25$ g of phenol
$= [15.67 \times (xV_1-V_2) \times w/(V_1 \times 0.3479 \times 20)]$ g of phenol $= 2.2521 \times (xV_1-V_2) \times w/V_1$ g of phenol

6. Estimation of aromatic amine (aniline) by bromination (Bromate-Bromide) method

Principle: Aniline reacts quantitatively with bromine to form a white precipitate of 2,4,6 tribromo aniline.



Thus 6000 mL (N) bromine ≡93·g of Aniline

So 1000 mL of (N) bromine ≡ (93/6) g i.e. 15.5 g of Aniline

Hence the equivalent weight of Aniline is 15.5

The Aniline solution is treated with measured excess of (KBr + $KBrO_3$) solution which is equivalent to bromine in acidic medium. The excess bromine is allowed to react with sufficient potassium iodide. Bromine oxidizes iodide to iodine. This iodine is estimated by titration against a standard solution of sodium thiosulfate. Thus, the amount of bromine left after consumption by phenol is determined. Difference between added and remaining bromine corresponds to the amount of phenol in the volume of sample solution taken for titration.

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 6KCl + 3H_2O$$
$$Br_2 + 2KI = 2KBr + I_2$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

1000 mL of (N) sodium thiosulfate ≡1000 mL of (N) iodine ≡ 1000 mL of (N) Br_2 ≡ 1000 mL of (N) aniline ≡15.5 g of aniline.

In acid medium bromate reacts according to the following equation

$$BrO_3^- + 6H^+ + 6e = Br^- + 3H_2O$$

So the equivalent weight of $KBrO_3$ = (molecular weight of $KBrO_3$/ 6) = (167/6) = 27.8334.

Chemicals required:

1. Standard (N/20) $KBrO_3$-KBr solution: Weigh out accurately ~ 0.35 g (w) (exactly 0.3479 g) of (A.R) **$KBrO_3$** and ~5 g of KBr in a 250 mL volumetric flask. Dissolve in distilled water and make up to the mark with distilled water.

2. Sodium thiosulfate solution: Dissolve·3-4 g of sodium thiosulfate pentahydrate in distilled water and dilute to 250 mL with distilled water.

3. 10% Potassium iodide solution

4. 1% Starch solution

5. Sample aniline solution: Dissolve 3-4 g of pure aniline in distilled water and dilute to one liter with distilled water. Dilute 20-25 mL of this stock solution to 100 mL with distilled water in a 100 mL volumetric flask. 25 mL of this diluted solution may be used for titration.

Procedure:

1. Standardisation of sodium thiosulfate solution against standard KBrO3-KBr solution: Pipette out 25 mL of standard $KBrO_3$-KBr solution in a 500 mL conical flask. Add 10 mL of 10% potassium iodide solution or 1 g of solid potassium iodide to this solution. Then add 5 mL conc. HCl to adjust the acidity to ~ 1.5(N). Cover the flask with a small watch glass and keep in dark for 3-4 minutes. Dilute with 100 mL of water to adjust the acidity of the resulting solution to ~ 0.5(N). Titrate the liberated iodine with sodium thiosulfate solution till the appearance of a straw yellow colour. Add 2 mL of 1 % starch solution when the solution

becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue colour. (end point: colourless)

2. Estimation of aniline: Transfer the sample aniline solution into a volumetric flask of definite size as directed and make up to the mark with distilled water.

Pipette out 25 mL of diluted phenol solution in a 500 mL conical flask. Add 10-12 mL of cone. HCl to maintain the acidity at ~ 3(N). Add a measured excess (25 x *x*) mL of standard $KBrO_3$-KBr solution so that a permanent yellow colour due to an excess of free bromine persists. Cover the flask with a small watch glass, shake well and allow to stand at room temperature in the dark for 5 minute with occasional shaking. Add 10 mL of 10% potassium iodide solution or 1 gm of solid potassium iodide. Dilute with 150 mL of distilled water adjust the acidity ~ 0.5(N). Titrate the liberate iodine with sodium thiosulfate solution till the appearance of a straw yellow colour. Add 2 mL of 1% starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue colour leaving white precipitate of 2,4,6 tribromo aniline in the solution.

1. Standardisation of sodium thiosulfate solution against standard $KBrO_3$-KBr solution:

Volume of $K_2Cr_2O_7$ (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of $KBrO_3$-KBr solution = (w/0.3479) (N/20)

So, the strength of sodium thiosulfate = S_1 = (25x w) / (V_1 x 0.3479) (N/20)

2. Estimation of aniline:

Volume of phenol solution (mL)	**Volume of KBrO3-KBr solution (mL)**	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_3)**
25	25 × x	x	
25	25 × y	y	(x + y+ z)/3
25	25 × z	z	

25 mL of $KBrO_3$-KBr solution ≡ V_1 mL S_1(N) $Na_2S_2O_3$ solution

So (25 × x) mL of $KBrO_3$-KBr solution ≡ (V_1 × x) mL S_1(N) $Na_2S_2O_3$ solution

Bromine left after consumption by aniline ≡ V_2 mL S_1(N) $Na_2S_2O_3$ solution

Hence bromine consumed by aniline ≡ (xV_1–V_2) mL S_1(N) $Na_2S_2O_3$ solution

Now 1000 mL of (N) $Na_2S_2O_3$ ≡ 15.5 g of aniline

So (xV_1–V_2) mL S_1(N) $Na_2S_2O_3$ ≡ [15.5 × (xV_1–V_2) × S_1]/1000 g of aniline

25 mL of aniline solution contains [15.5 × (xV_1–V_2) × S_1]/1000 g of aniline

So 1000 mL of aniline solution contains [15.5 × (xV_1–V_2) × S_1]/(25)g of aniline

= [15.5 × (xV_1–V_2) × w/(V_1 × 0.3479 × 20)] g of aniline = 2.2276 × (xV_1–V_2) × w/V_1 g of aniline

7. Estimation of Formaldehyde (Formalin)

Principle: Formaldehyde is quantitatively oxidized by iodine in weakly alkaline medium to formate.

$$HCHO + I_2 + 3\,HO^- \rightleftharpoons HCO_2^- + 2\,I^- + 2\,H_2O$$

Thus 2000 mL (N) iodine ≡ 30 g of formaldehyde

So 1000 mL (N) iodine ≡ 15 g of formaldehyde

A known volume of formalin solution is allowed to react with a measured excess of iodine solution. The iodine left after consumption by titration against a standard solution of sodium thiosulfate. Thus the amount of iodine left after consumption of formalin is determined. Difference between added and remaining iodine corresponds to the amount of formalin in the volume of sample solution taken for titration.

Thus 1000 mL sodium thiosulfate ≡1000 mL of (N) iodine ≡ 1000 mL of (N) formalin ≡ 15 g of formalin.

Chemicals required:

1. Standard (N/20) $K_2Cr_2O_7$ solution: Weigh out accurately ~ 0.6129 g (w) of (A.R) $K_2Cr_2O_7$ in 250 mL volumetric flask, dissolve in distilled water and make up to the mark with distilled water. Mix the solution uniformly.

2. (N/20) I_2 solution: Mix~ 1.6 g of solid iodine 2 g of potassium iodide. Add 10-15 rnL of water and stir to dissolve. Dilute the solution to 250 mL with distilled water.

3. (N/20) sodium thiosulfate solution: Dissolve 3-4 g of sodium thiosulfate pentahydrate in distilled water dilute to 250 mL and mix uniformly.

4. 10% potassium iodide solution.

5. 1% Starch Indicator.

6. Sample formalin solution: Dissolve 4-5 mL of formalin in distilled water, dilute to one litre with distilled water.

Procedure:

1. Standardization of sodium thiosulfate solution against standard potassium dichromate solution: Pipette out 25 ml of standard (N/ 20) $K_2Cr_2O_7$ solution in a 500 mL conical flask Add 25 mL of 4(N) sulfuric acid and 10 mL of 10% Kl (or 1 g of solid KI) solution to it. Cover the flask with a small watch glass and allow to stand in dark for 4-5 minutes. Dilute with 150 mL of distilled water to adjust the acidity to ~ 0.5(N). Titrate with sodium thiosulfate solution till the appearance of a straw yellow color. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the blue color disappears with the appearance of a light green color.

2. Standardisation of iodine solution against standard sodium thiosulfate solution : Pipette out 25 mL of iodine solution in a 500 mL conical flask. Add 75 mL of distilled water to it. Titrate with standard sodium thiosulfate solution till the appearance of a straw yellow colour. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue colour. (end point :colourless)

3. Estimation of formalin: Transfer quantitatively the sample formalin solution into a volumetric flask of definite size as directed and make up to the mark with distilled water. Shake well to ensure uniform mixing.

Pipette out 25 mL of the unknown formalin solution in a 500 mL conical flask. Add 25 mL of standard iodine solution so that the color of iodine persist in solution. Then add 5% NaOH solution drop wise till the solution assumes light yellow color and this yellow color persists after keeping the mixture for 15 minutes. After that add 15 mL of 5%HCl solution. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Titrate against standard sodium thiosulfate solution till the disappearance of the blue colour. (end point: colourless).

Results:

1. Standardization of sodium thiosulfate solution against standard potassium dichromate Solution:

Volume of $K_2Cr_2O_7$ (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of $K_2Cr_2O_7$ solution = (w/0.6129) (N/20)

So the strength of $Na_2S_2O_3$ solution = (25 x w) / (V_1 x 0.6129) (N/20)

2. Standardization of iodine solution against standard sodium thiosulfate solution:

Volume of I_2 (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_2)**
25	x	
25	y	(x + y+ z)/3
25	z	

3. Estimation of formalin solution:

Volume of formalin solution (mL)	**Volume of I_2 solution (mL)**	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_3)**
25	25 × x	d	
25	25 × y	e	(d + e+ f)/3
25	25 × z	f	

Calculation:

25 mL of iodine solution ≡ V_2 mL of S_1 (N) sodium thiosulfate solution

So (25×x) mL of iodine solution ≡ (V_2× x) mL of S_1 (N) sodium thiosulfate solution

Hence iodine consumed by formalin ≡ (xV_2-V_3) mL of S_1 (N) sodium thiosulfate solution

now 1000 mL of (N) thiosulfate ≡ 1000 mL of (N) iodine ≡ 1000 mLof (N) formalin ≡ 15 g of formalin.

So (xV_2-V_3) mL of S_1 (N) sodium thiosulfate solution ≡ [15 × (xV_2-V_3)×S_1 (N)]/1000 g of formalin= [15 × (xV_2-V_3)×25×w]/(1000×V_1×0.6129×20) g of formalin

Thus 25 mL of formalin solution contains = [15 × (xV_2-V_3)×25×w]/(1000×V_1×0.6129×20) g of formalin

Hence 10000mL of formalin solution contains = [15 × (xV_2-V_3)×25×w]/(1000×V_1×0.6129×20) g of formalin

= 1.224 × [(xV_2-V_3)×w]/(V_1) g of formalin.

8. Estimation of Acetic acid in commercial vinegar

Commercial vinegar contains 4-8% (v/v) acetic acid. Acetic acid, a weak acid, can be estimated by titration against a strong alkali like sodium hydroxide.

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

Chemicals required:

1. Standard (N/20) oxalic acid solution: Weigh out accurately~ 0.8 g (w) (exactly 0.7879 g) of A.R oxalic acid, dissolve it in distilled water in a 250 mL volumetric flask and make up the volume with distilled water up to the mark. Mix well to ensure homogeneity of the solution.

2. **(N/20) NaOH solution:** Dissolve ~1 g of solid NaOH in 500 mL of distilled water.

3. **Phenolphthalein indicator:** 0.5% in (1:1) ethanol

4. Sample commercial vinegar solution: Mix 75-80 mL of commercial vinegar in distilled water and dilute to one litre with distilled water.

Procedure:

1. **Standardization of NaOH against Standard oxalic acid solution**: Pipette out 25 mL of standard oxalic acid solution in a 250 mL conical flask. Add 2-3 drops of phenolphthalein indicator. Add NaOH solution from a burette until the appearance of a faint pink color.

2. Estimation of acetic acid: Dilute the supplied vinegar solution as directed. Pipette out 25 mL of the dilute unknown vinegar solution in a 250 mL conical flask. Add 2-3 drops of phenolphthalein indicator. Add NaOH solution from burette until the appearance of a faint pink color.

Results:

1. Standardization of sodium hydroxide solution against standard oxalic acid:

Volume of oxalic acid (mL)	**Volume of NaOH (mL)**	**Mean volume of NaOH (mL) (V_1)**
25	a	
25	b	(a+b+c)/3

25	c	

Strength of oxalic acid solution = (w/0.7879) (N/20)

So the strength of NaOH solution = (25 x w) / (V_1 x 0.7879) (N/20)

2. Estimation of acetic acid in vinegar:

Volume of vinegar (mL)	**Volume of NaOH (mL)**	**Mean volume of NaOH (mL) (V_2)**
25	x	
25	y	(x + y+ z)/3
25	z	

Calculation:

1000 mL of (N) NaOH ≡ 1000 mL of (N) acetic acid ≡ 60 g of acetic acid

So V_2 mL of S_1 (N) NaOH ≡ $(60\times V_2\times S_1)/1000$ g of acetic acid

Thus 25 mL of formalin solution contains $(60\times V_2\times S_1)/1000$ g of acetic acid

Hence 1000 mL of vinegar solution contains $(40\times 60\times V_2\times S_1)/1000$ g of acetic acid

$= [40 \times 60\times V_2\times 25\times w]/(V_1\times 0.7879\times 20)$ g of acetic acid

$= 3.8076 \times (wV_2/V_1)$ g of acetic acid

9. Estimation of Saponification value of oil

Principle: Saponification value of an oil/fat/ester is the number of milligrams of KOH needed to completely saponify 1 g of oil/fat/ester. A weighed quantity of oil/fat/ester is completely saponified by boiling with a measured excess of standard alcoholic KOH solution. The excess KOH is then back titrated against a standard HCl solution.

1000 mL of (N) HCl solution ≡1000 mL of (N) KOH solution ≡ 56 g of KOH

So 1 mL of (N) HCl solution ≡1 mL of (N) KOH solution ≡ 56 mg of KOH

Chemicals required:

1. Standard (N/20) oxalic acid solution: Weigh out accurately~ 0.8 g (w) (exactly 0.7879 g) of A.R oxalic acid, dissolve it in distilled water in a 250 mL volumetric flask and make up the volume with distilled water up to the mark. Mix well to ensure homogeneity of the solution.

2. **Coconut oil or mustard oil.**

3. (N/2) alcoholic KOH solution: Dissolve ~7.0 g of KOH in minimum volume of distilled water. Dilute to 250 mL with ethanol. Then dilute 10 mL of this solution to 100 mL in a 100 mL volumetric flask to prepare ~ (N/20) KOH solution.

4. (N/2) HCl solution: Dilute 10-12 mL of conc. HCl to 250 mL with distilled water and dilute to 10 mL of this solution to 100 mL in a 100 mL volumetric flask to prepare ~(N/20) HCl solution.

Procedure:

1. **Standardization of KOH against Standard oxalic acid solution**: Pipette out 25 mL of standard oxalic acid solution in a 250 mL conical flask. Add 2-3 drops of phenolphthalein indicator. Add KOH solution from a burette until the appearance of a faint pink color.

2. Standardization of HCl against Standard KOH solution: Pipette out 25 mL of ~(N/20) HCl solution in a 250 mL conical flask. Add 2-3 drops of phenolphthalein indicator. Add KOH solution from a burette until the appearance of a faint pink color.

3. Estimation of saponification value: Weigh out accurately ~2.0 g of coconut or mustard oil in a 250 mL conical flask fitted with an air condenser. Add 50 mL of standard ~ (N/2) alcoholic solution to it. Reflux the resulting solution on a hot water bath till the complete disappearance of the oily layer. Allow the mixture to cool to room temperature and add 2-3 drops of phenolphthalein indicator to it. The solution turns pink. Titrate the unreacted KOH by the standard (N/2) HCl solution till the disappearance of the pink color forming a colorless solution.

Results:

1. Standardization of potassium hydroxide solution against standard oxalic acid:

Volume of oxalic acid (mL)	**Volume of KOH (mL)**	**Mean volume of KOH (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of oxalic acid solution = (w/0.7879) (N/20)

So the strength of KOH solution = (25 x w) / (V_1 x 0.7879) (N/20)

Hence the exact strength of (~N/2) KOH solution = S_1= (25 x w) / (V_1 x 0.7879) (N/2)

2. Standardization of HCl solution against standard potassium hydroxide:

Volume of HCl (mL)	**Volume of KOH (mL)**	**Mean volume of KOH (mL) (V_2)**
25	x	
25	y	(x + y+ z)/3
25	z	

So the strength of HCl solution = [(25 x w) / (V_1 x 0.7879) (N/20)]× V_2/25

= [(V_2× w) / (V_1 x 0.7879)] (N/20)

Hence the exact strength of (~N/2) HCl solution = S_2= [(V_2× w) / (V_1 x 0.7879)] (N/2)

3. Estimation of the saponification value:

Weight of mustard/ coconut oil (g)	**Volume of (N/2) KOH (mL)**	**Mean volume of (N/2) HCl (mL) (V_3)**
w_1	50	V_3

4. blank experiment:

Volume of (N/2) KOH (mL)	**Mean volume of (N/2) HCl (mL) (V_4)**
50	V_4

Calculation:

V_4 mL S_2 (N) HCl is needed for 50 mL of S_1 (N) KOH.

V_3 mL S_2 (N) HCl is needed for back titration of S_1 (N) KOH after consumption by w_1 g of oil/fat/ester.

Hence KOH consumed by w_1 g of oil/fat/ester $\equiv (V_4-V_3)$ mL of $(V_2 \times w/0.7879 \times V_1)(N/2)$ HCl.

$\equiv (V_4-V_3)$ mL of $[(V_2 \times w)/(0.7879 \times V_1)](N/2)$ KOH.

$\equiv [(V_4-V_3) \times V_2 \times w]/(2 \times 0.7879 \times V_1)$ mL (N) KOH

$\equiv [56 \times (V_4-V_3) \times V_2 \times w]/(2 \times 0.7879 \times V_1)$ mg of KOH

[As 1 mL of (N) KOH ≡ 56 mg of KOH].

Thus saponification value of the oil/fat/ester

= number of milligrams of KOH consumed by 1.0 g of oil/fat/ester

$= [56 \times (V_4-V_3) \times V_2 \times w]/[2 \times w_1 \times 0.7879 \times V_1]$

10. Estimation of urea

Principle: Urea is quantitatively oxidized by hypobromite in the presence of alkali.

$$CO(NH_2)_2 + 3^-OBr + 2\ ^-OH = N_2 + 3\ Br^- + CO_3^{2-}$$

An aqueous solution of urea is treated with a measured excess of standard alkaline solution of hypobromite. Unreacted hypobromite is then allowed to react with an excess of potassium iodide solution in the presence of dilute sulfuric acid in cold. The liberated iodine is then back titrated against a standard solution of sodium thiosulfate.

$$^-OBr + 2I^- + 2H^+ = I_2 + Br^- + H_2O$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

So,

$$^-OBr \equiv I_2 \equiv 2S_2O_3^{2-} \text{ and } CO(NH_2)_2 \equiv 3^-OBr \equiv 3I_2 \equiv 6\ S_2O_3^{2-}$$

Thus, 1000 mL of (N) $Na_2S_2O_3$ ≡ (molecular weight of urea /6) g of urea ≡ (60/6) g ≡ 10 g of urea.

Hypochlorite is unstable when prepared directly from bromine and alkali. Hence it is prepared in the reaction medium using an excess of bromide and a solution of hypochlorite.

Chemicals required:

1. Standard (N/20) $K_2Cr_2O_7$ solution: Weigh out accurately ~ 0.6129 g (w) of $K_2Cr_2O_7$ in a 250 mL volumetric flask, dissolved in distilled water and make up to the mark with distilled water. Mix the solution uniformly.

2. (N/20) $Na_2S_2O_3$ solution: Dissolve 3-4 g of $Na_2S_2O_3$ in distilled water, dilute to 250 mL and mix uniformly.

3. l0% potassium iodide solution.

4. (N/20) calcium hypochlorite solution.

5. 1% Starch indicator. . . .

6. Sample urea solution: Dissolve ~ 0.4-0.5 g of urea in one litre of distilled water.

Procedure:

1. Standardization of sodium thiosulfate solution against standard potassium dichromate solution:

Pipette out 25 mL of standard (N/20) $K_2Cr_2O_7$ solution a 500 mL corneal flask. Add 25 mL of 4(N) sulfuric acid and 10 mL of 10% KI (or 1 g of solid KI) solution to it. Cover the flask with a small watch glass and allow to stand in ·dark for 4-5 minutes. Dilute with 150 mL of distilled water to adjust the acidity to ~ 0.5 (N). Titrate with sodium thiosulfate solution till the appearance of a straw yellow color. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue color with the appearance of a light green color.

2. Preparation of (N/20) calcium hypochlorite solution:

Shake thoroughly 1-2 g of bleaching powder with 100 mL of distilled water in a 250 mL conical flask. Filter the slurry through a Whatman No. 1 filter paper to remove iron oxide, excess of calcium hydroxide and any other insoluble material. Dilute the filtrate with distilled water up to 250 mL mark in the flask.

3. Standardization of hypochlorite solution:

Take an aliquot of 25 mL of hypochlorite solution in a 500 mL conical flask. Add 25 mL of 4(N) sulfuric acid and ~ 2g o£ solid potassium iodide and cover the flask with a small watch glass and keep the solution in dark for 3-4 minutes. Dilute with 150 mL of distilled water. Titrate with sodium thiosulfate solution till the appearance of a straw yellow color. Add 2 mL of 1 % starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue color.

4. Estimation of Urea:

Pipette out 25 mL of the unknown urea solution in a 500 mL of conical flask. Add 2 g of potassium iodide and 0.5 g of sodium carbonate. Shake thoroughly to ensure complete dissolution of the added salts (KBr and $NaHCO_3$). Add a measured excess of standard

hypochlorite solution (let 25 mL x *x*) till a permanent yellow color due to free Br persists in the solution. Cover the flask with a small watch glass allow to stand for 5 minutes. Then slowly add 10 ml of 6 (N) sulfuric acid to the solution followed by addition of 1 g of solid KI. Cover the flask with a small watch glass and keep the solution in dark for 3-4 minutes. Dilute to ~ 200 mL with distilled water. Titrate the liberated iodine with standard sodium thiosulfate solution till the appearance of a straw yellow color. Add 2 mL of 1% starch solution when the solution becomes intense blue. Continue addition of sodium thiosulfate till the disappearance of the blue color.

Results:

1. Standardization of sodium thiosulfate solution against standard potassium dichromate Solution:

Volume of $K_2Cr_2O_7$ (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_1)**
25	a	
25	b	(a+b+c)/3
25	c	

Strength of $K_2Cr_2O_7$ solution = (w/0.6129) (N/20)

So the strength of $Na_2S_2O_3$ solution = (25 x w) / (V_1 x 0.6129) (N/20)

2. Standardization of hypochlorite solution:

Volume of hypochlorite (mL)	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_2)**
25	x	
25	y	(x + y+ z)/3
25	z	

3. Estimation of Urea:

Volume of urea solution (mL)	**Volume of hypochlorite (mL)**	**Volume of $Na_2S_2O_3$ (mL)**	**Mean volume of $Na_2S_2O_3$ (mL) (V_3)**
25	25 × x	d	
25	25 × y	e	(d + e+ f)/3
25	25 × z	f	

Calculation:

25 mL of hypochlorite solution ≡ V_2 mL of S_1(N) sodium thiosulfate solution

So (25 × x) mL of hypochlorite solution ≡ ($V_2 \times x$) mL of S_1(N) sodium thiosulfate solution

Thus hypochlorite (i.e hypobromite) consumed by urea ≡ ($xV_2 - V_3$) mL of S_1(N) sodium thiosulfate solution

Now 1000 mL of (N) thiosulfate ≡ 10 g of urea

So (xV_2–V_3) mL of S_1(N) sodium thiosulfate ≡ [10 × (xV_2–V_3)S_1]/1000 g of urea

= [10 × (xV_2–V_3)25 × w]/(1000 × V_1 × 0.6129 × 20)g of urea

Thus 25 mL of urea solution contains = [10 × (xV_2–V_3)25 × w]/(1000 × V_1 × 0.6129 × 20)g of urea

Hence,

1000 mL of urea solution contains = [10 × (xV_2–V_3) × 1000 × w]/(1000 × V_1 × 0.6129 × 20)g of urea

= [0.8158 × (xV_2–V_3) × w]/(V_1)g of urea

GE4: Lab

Experiment 1: Determination of dissociation constant of a weak acid

Theory:

Electrolytes obey Ohm's law i.e.,

Current (I) ∝ Voltage (V) applied

The proportionality constant is called conductance (C) [inverse of resistance (R)] of the conductor concerned. The conductance of an electrolyte solution is measured with the help of a conductivity cell. If two parallel electrodes, each of area 'A' are placed 'I' distance apart then the measured conductance (C) of an electrolyte solution will be

C= $\frac{1}{R} = \frac{1}{\rho}\frac{A}{l}$, ρ is the resistivity

= k $\frac{A}{l}$, k is the specific conductance or conductivity of the electrolyte solution.

Or, k = C$\frac{l}{A}$, Where $\frac{l}{A}$ is called cell constant of the conductivity cell

i.e., Specific conductance = Conductance × Cell constant

The specific conductance (k) of an electrolyte solution is its conductance when unit volume of the solution is placed between two parallel electrodes each of unit area and set unit distance apart. In C.G.S. its unit is ohm^{-1} cm^{-1}.

Cell constant of a conductivity cell is determined by measuring the conductance of an electrolyte solution of known specific conductance at the experimental temperature within the same conductivity cell.

Equivalent conductance (λ) of an electrolyte solution is its conductance associated with a definite volume of the solution containing 1 gm equivalent of the electrolyte placed between two large electrodes set unit distance apart. Therefore,

Equivalent conductance (λ) = Specific conductance (k) × volume of the solution in cm^3 containing 1 gm equivalent of the electrolyte

Unit of 'λ' in CGS in $ohm^{-1}cm^2g\ equi^{-1}$.

Equivalent conductance of a weak electrolyte will increase with dilution and this is mainly due to increase n degree of dissociation, the variation of ionic mobility with dilution being insignificant due to low concentration of the ions.

Let α be the degree of ionization of a weak acid HA at concentration C equivalent/lit.

Then at equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

The dissociation constant or ionization constant (K_a) can be represented as

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If equivalent conductance of the weak electrolyte at concentration/ lit and at infinite dilution are λ and λ_0 respectively then,

$$\alpha = \frac{\lambda}{\lambda_0}$$

$$\text{so, } K_a = \frac{C(\lambda/\lambda_0)^2}{1-\frac{\lambda}{\lambda_0}}$$

$$\text{or, } 1-\frac{\lambda}{\lambda_0} = \frac{C\lambda^2}{K_a{\lambda_0}^2} \qquad \text{or, } \frac{1}{\lambda} = \frac{1}{\lambda_0} + \frac{\lambda C}{{\lambda_0}^2 K_a}$$

This is known as Ostwald dilution law. The plot of $\frac{1}{\lambda}$ vs. λC will be a straight line with a positive intercept $\frac{1}{\lambda_0}$ from which λ_0 can be calculated. From the slope $\frac{1}{{\lambda_0}^2 K_a}$, K_a can be calculated using the temperature corrected literature value of λ_0.

Apparatus required:

9) 100ml vol. flask -3
10) 250ml conical flask -1
11) 100ml beaker -2
12) 500ml glass bottle -2
13) Burette -1
14) Pipette 25 ml -2

15) Pipette 10ml -1
16) 250ml vol. flask -2

Chemicals required:

Oxalic acid, Acetic acid, NaOH, KCl, Phenolphthalein

Procedure:

10) Prepare 100ml ~(N/10) oxalic acid solution by accurate weighing.
11) Prepare approximately 250ml of ~(N/10) NaOH solution and standardize the NaOH solution against the prepared standard oxalic acid solution.(use phenolphthalein).
12) Prepare 250ml of ~(N/10) acetic acid solution in conductivity water and standardize the solution against the standard NaOH solution (use phenolphthalein).
13) Prepare 250ml ~ 0.1 (N) [slightly higher than 0.1 (N) KCl solution by accurate weighing and prepare 100ml of an exact 0.1 (N) KCl solution by proper dilution. Prepare 100ml of an exact 0.01 (N) KCl from the exact 0.1 (N) KCl solution. Determine the cell constant of the conductivity cell using the exact 0.1 (N) KCl and the prepared exact 0.01 (N) KCl solution .With the help of the literature value of specific conductances of these solutions at room temperature, calculate the mean value of cell constant and use it subsequently. Measure the conductance of conductivity water also.
14) Prepare 250ml, exact (N/50) weak acid solution from the standardized solution using conductivity water. With the help of 25ml pipette, take 50ml of this solution in the clean and dry conductivity cell and measure its conductance.
15) Use the same 25ml pipette to take out 25ml of the (N/50) weak acid solution from the conductivity cell. Pipette out 25ml of the conductivity water into the conductivity cell to make the solution exactly (N/100) in situ. Mix the solution well by careful swirling (so that no solution comes out). Measure the conductance and note it as that of exact (N/100) weak acid solution. Separate pipettes for weak acid solutions and conductivity water may be used.
16) Follow the procedure of step (6) to prepare in situ exact (N/200), (N/400), (N/800), and (N/1600) weak acid solutions in steps and note their conductances.
17) Calculate the equivalent conductivities of the diluted solutions of the weak acid using the mean value of cell constant. Apply corrections for specific conductance of conductivity water.
18) From the plot of $1/\lambda$ versus (λC) calculate the λ_0 from the intercept and from the temperature corrected literature value of ion conductances. Calculate K_a and pk_a of the weak acid from the slope using the temperature corrected literature value of λ_0.

Experimental result:

12) Room temperature.
13) Preparation of 100ml 0.1(N) oxalic acid.
14) Preparation of 250ml approximately 0.1(N)NaOH solution.
15) Standardisation of NaOH solution against standard oxalic acid solution:

Volume of oxalic acid (ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of NaOH solution: …….

16) Preparation of 250ml ~(N/10) acetic acid solution:

17) Standardisation of acetic acid solution against standard NaOH solution :

Strength of acetic acid solution:

Volume of acetic acid solution(ml)	Burette reading		Volume of NaOH used	Average volume of NaOH (ml)
	Initial(ml)	Final(ml)		
10				
10				

18) Preparation of 250ml exact (N/50) acetic acid solution.
19) Preparation of 250ml ~0.1 (N) [slightly higher than 0.1 (N) KCl solution.
20) Preparation of 100ml exact 0.1 (N) KCl solution and preparation of exact 0.01 (N) KCl .
21) Determination of cell constant:

Concentration of KCl solution	Conductance (mho)	Specific conductance ($mho.cm^{-1}$)	Cell constant (cm^{-1})	Mean cell constant (cm^{-1})
0.01(N)				
0.1(N)				

22) Determination of equivalent conductance of different acetic acid solutions:

Concentration of acetic acid solution	Observed conductance (mho)	Corrected specific conductance ($mho.cm^{-1}$) {Observed conductance- Conductance of conductivity water) × mean cell constant}	Equivalent conductance (λ) ($mhocm^2eq^{-1)}$	1/ λ ($mho^{-1}cm^{-2}eq$)	Λc($mhocm^{-1}$)

The plot of $\frac{1}{\lambda}$ vs λC will be a straight line with a positive intercept $\frac{1}{\lambda_0}$ from which λ_0 can be calculated.

From the slope $\frac{1}{\lambda_0{}^2 K_a}$, K_a can be calculated using the temperature corrected literature value of λ_0.

Temperature corrected literature value of $\lambda_0 = \lambda_t^0 (H^+) + \lambda_t^0 (OAc^-)$

$$\lambda_t^0 (H^+) = \lambda_{25}^o [1+1.42\times 10^{-2} (t-25)]$$

$$\lambda_t^0 (OAc^-) = \lambda_{25}^o [1+0.02 (t-25)]$$

Experiment 2: Potentiometric titration of Mohr's salt solution against standard K2Cr2O7 solution:

Theory:

The electrode potential (half cell potential) associated with an electrode process (half cell process),

$$\nu_A A + \nu_B B + \cdots .. = \nu_L L + \nu_M M + \cdots + ne$$

is given according to Nernst equation by

$E = E^0 - \frac{RT}{nF} \ln \frac{a_L^{\nu_L}}{a_A^{\nu_A}} \frac{a_M^{\nu_M} \ldots}{a_B^{\nu_B} \ldots}$, where the terms have their usual significance.

If Fe^{3+}/Fe^{2+} redox system is coupled with a saturated calomel electrode (SCE), as the reference electrode, the following electrochemical cell is produced :

$$Pt \,|\, Hg(l) \,|\, Hg_2Cl_2(s) \,|\, KCl(sat., aq) \,||\, Fe^{2+}(aq), Fe^{3+}(aq) \,|\, Pt$$

where | | represents agar-KCl salt bridge used to minimize the liquid junction potential.

Electrode processes can be represented as :

Small **Anode (LHE) :** $2Hg\,(l) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s) + 2e$

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

Overall electrode potential (EMF) of the cell (E_{cell}) is given by,

$E_{cell} = E_R - E_L = E^0_{Fe^{3+}|Fe^{2+}} + \frac{2.303RT}{F} \log\{[Fe^{3+}]/[Fe^{2+}]\} - E_{SCE}$, where E_R and E_L both represents reduction potential of the respective electrode.

If temperature remains constant, E_{SCE} remains unchanged and E_{cell} varies with change in the ratio $\{[Fe^{3+}]/[Fe^{2+}]\}$. With gradual addition of an oxidant like $K_2Cr_2O_7$ to a solution of Fe^{2+} in acid medium, the ratio $\{[Fe^{3+}]/[Fe^{2+}]\}$ progressively increases and consequently E_{cell} increases. Near the equivalence point the ratio $\{[Fe^{3+}]/[Fe^{2+}]\}$ increases rapidly on adding even a very amount of oxidant and at equivalence point there will be a sharp jump in the value of E_{cell}. After equivalence point further addition of oxidant results in a small increase in E_{cell}.

A potentiometric curve is obtained on plotting E_{cell} vs volume (number of drops) of standard solution of oxidant ($K_2Cr_2O_7$) added to a known volume of Mohr's salt solution in acid medium. The standard electrode potential ($E^0_{Fe^{3+}|Fe^{2+}}$) of Fe^{3+}/Fe^{2+} Redox system can be determined from the graph as follows:

At the half equivalence point $[Fe^{3+}] = [Fe^{2+}]$ and $E_{cell} = E_{1/2}$ $E^0_{Fe^{3+}|Fe^{2+}} - E_{SCE}$

Or, $E^0_{Fe^{3+}|Fe^{2+}} = E_{1/2} + E_{SCE}$

From the half equivalence point $E^0_{Fe^{3+}|Fe^{2+}}$ E_{SCE}, at room temperature may be obtained.

From the inflection point of the graph volume of oxidant required to completely oxidize Fe^{2+} is obtained and from the known volume of Mohr's salt solution, its strength can be calculated using the relation, $V_{Mohr} \times S_{Mohr} = V_{Dichromate} \times S_{Dichromate}$.

Apparatus required:

1) 100 mL vol.flask-1

2) 100 mL beaker-1
3) Burette-1
4) Pipette 10 mL-1
5) 250 mL Glass bottle-1
6) Potentiometer with reference calomel electrode and agar-KCl salt bridge
7) Platinum electrode

Chemicals required: Mohr's salt, $K_2Cr_2O_7$, 2(N) sulphuric acid.

Procedure:

1) Dissolve about 2 g Mohr's salt in 100 mL 2(N) sulphuric acid solution to prepare Mohr salt solution (~N/20).
2) Prepare 100 mL of a standard (N/2) $K_2Cr_2O_7$ solution by exact weighing. Take the prepared standard (N/2) solution $K_2Cr_2O_7$ in a burette. Determine the volume of 50 drops and calculate the volume of one drop.
3) Standardize, the potentiometer with a standard cell.
4) Take an aliquot of 10 mL of the prepared~(N/20) solution of Mohr salt in a 100 mL beaker. Add sufficient amount of~(2N) H_2SO_4 in the beaker, homogenize and dip a clean platinum electrode into the solution. Connect this half cell with the saturated calomel electrode through an agar-KCl salt bridge.
5) Measure the EMF of the experimental cell.
6) Add the (N/2) $K_2Cr_2O_7$ solution from the burette drop wise into the solution taken in the beaker, stir gently and measure the EMF each time. Take at least 4 readings after the end point.
7) Plot the EMF (E_{cell}) versus the total number of drops of $K_2Cr_2O_7$ solution added.
8) Find the $E^0_{Fe^{3+}|\,Fe^{2+}}$ at room temperature and the concentration of Mohr's salt solution from the graph using literature value of E_{SCE}.

E_{SCE} (at t^o C) =[0.2415-0.00076(t-25)] volt.

Experimental result:

1) Room temperature.
2) Preparation of 100 mL Mohr's salt solution (~N/20).
3) Preparation of 100 mL (N/2) solution.
4) 50 drops of $K_2Cr_2O_7$ solution = …….mL $K_2Cr_2O_7$
5) Potentiometric titration of (~N/20) Mohr's salt solution vs (N/2) $K_2Cr_2O_7$ solution:

Volume of (N/20) Mohr's salt solution	**No. of drops of $K_2Cr_2O_7$ solution added**	**Total no. of drops $K_2Cr_2O_7$ solution added**	**E_{cell} (volt)**

10 mL			

Graph Plotting:

Plot the EMF (E_{cell}) vs the total number of drops of $K_2Cr_2O_7$ solution added. From the inflection of the graph find the number of drops of $K_2Cr_2O_7$ solution and hence the volume corresponds to the equivalence point. Fine the $E_{1/2}$ corresponding to the half equivalence point.

Calculation:

At equivalence point,… drop $K_2Cr_2O_7$ solution= …ml $K_2Cr_2O_7$ = $V_{Dichromate}$

Strength of Mohr's salt solution (S_{Mohr}) = ($V_{Dichromate}$× $S_{Dichromate}$)/V_{Mohr}

At the half equivalence point,

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

Precautions and suggestions:

1) Initially add 2 drops of oxidant solution at a time up to total 10 drops and then add 1 drop at a time till equivalence point is reached. Stir gently so that no solution comes out of the beaker.
2) The total number of drops of oxidant (and hence volume) corresponding to the end point may also be known from the maximum of the plot of $\frac{|\Delta E_{cell}|}{\Delta n}$ vs n (mean of the total number of drops corresponding to $\frac{|\Delta E_{cell}|}{\Delta n}$.

Experiment 3: Study of phenol-water phase diagram

Theory:

The minimum number of intensive variables (e.g. temperatures, pressure, concentration of constituents in each phase etc.) that must be specific to describe completely the state of an

equilibrated system is called the number of degrees of freedom (F) of the system. This is represented by the following relationship,

$$F = C-P+2$$

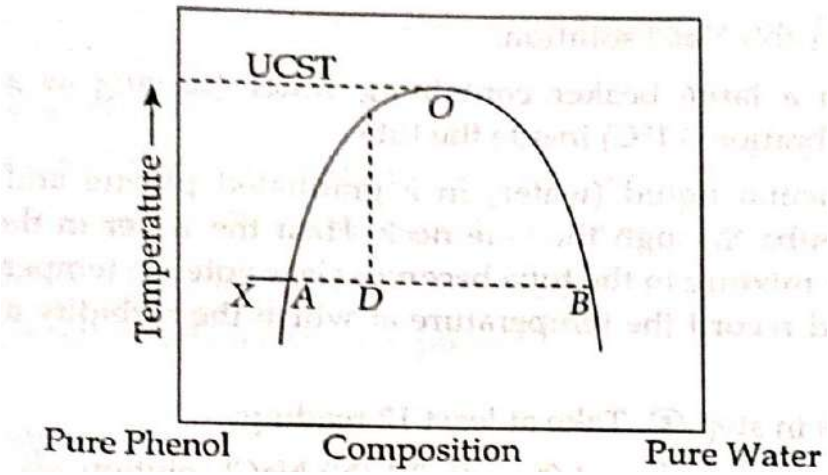
Where, 'p' is the number of kinds of phases in equilibrium and 'C' is the number of components of the system.

Any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces is called a phase of the system.

The minimum number of chemical species (constituents) required to describe the composition of each phase of a system is called the number of components (C) of the system and is equal to the total number of constituents (N) minus the no of independent chemical equilibrium expression (R) minus the number of independent additional restricting equilibrium (R') due to material balance or charge within each phase, i.e, **C=N-R-R'.**

When two partially miscible liquids (pairs of liquids miscible with each other in limiting range of concentrations) are mixed, at a certain stage we get two solutions of different compositions. For example on shaking phenol and water within the partially miscible range we get two phases (layers): (i) a saturated solution of phenol in water, and (ii) a saturated solution of water in phenol. These two solutions of different compositions existing in equilibrium with one another are known as conjugate solutions. The compositions of these solutions are fixed and are independent of the relative amounts of the two phases. On gradual addition of one constituent to the other at a particular temperature, a stage is reached when the two phases system becomes one phase system (unsaturated solution of one constituent in the other). Also as temperature is raised the compositions of the two solutions become closer due to the increase in mutual solubility of the two constituents. At a certain temperature an pressure, the compositions of the two solutions become identical, thereby forming a single solution. Such a temperature is known as the Critical Solution Temperature (CST) or Consolute Temperature. As the mutual solubility increases with temperature in this particular case. It is known as Upper Consolute Temperature. This is observed in case of phenol-water system.

If compositions of the two solutions and the corresponding temperature is plotted, we obtain a curve of the type shown below



For this system solubility is studied at constant pressure. Therefore F= C-P+2-1 = C-P+1

At a point (say X) outside the solubility curve AOB we have P=1 and C=2.

So, F=2-1+1=2 i.e, both temperature and composition of the solution should be stated in order to define the system.

At a point (say D) inside the solubility curve or on the solubility curve (say A or B) we have P=2 and C=2

So, F=2-2+1=1 i.e, the value of only one variable (temperature or composition) is needed in order to define the system.

At critical solution temperature (CST), the compositions of the two solution become identical ad due to this additional restriction number of components (C) become 1. Thus, we have F=1-2+1=0 i.e. the critical solution temperature and the corresponding composition have fixed valued for a given value of pressure (usually 1 atm.)

Effect of impurity on CST:

If any substance is added as impurity into the mixture, the number of components at CST become two i.e. F=2-2+1=1. Hence CST become variable in the experimental condition. If the impurity is soluble in one of the liquid CST increases and if it is soluble I both in both the liquids CST decrease.

Apparatus required:

1) Apparatus for phase experiment.
2) Thermometer with 0.1ºC graduations
3) Heating arrangement
4) Graduated pipette(1mL)
5) 500 mL beaker -1
6) Weighing bottle-small
7) 100 mL volumetric flask

Chemicals required: Phenol, NaCl

Procedure:

1) Weight out accurately about 4 gm of phenol from a weighing bottle to a hard glass tube with a side neck.
2) Prepare 100 mL 0.1(N) NaCl solution.
3) Place the tube in a large beaker containing water (serving as a water bath). Insert a thermometer (calibration 0.1ºC) inside the tube
4) Take experimental liquid (water) in a graduated pipette and add 1.0 ml of water to phenol in the tube through the side neck. Heat the water in the beaker with constant stirring. When the mixture in the tube becomes clear note the temperature. Allow the whole system to cool and record the temperature. Allow the whole system to cool and record the temperature at which the turbidity appears. Take the mean temperature.
5) Repeat the process in step (4) Tae at least 12 readings.
6) Repeat the process in step (4) and (5) with 0.1(N) NaCl solution.
7) Find the weight percentage of phenol in the mixture at each of the temperature noted. Assume the density of water and 0.1(N) NaCl solution to be 1.0 g/mL.

(8) Find the critical solution temperature and corresponding composition from the phase diagram obtained by plotting the mean temperature (of disappearance and appearance of turbidity) versus weight percent of phenol for both cases and 0.1(N) NaCl solution.

Experimental result:

1) Room temperature:
2) Weight of phenol:
3) Table 1: Determination of CST for phenol-Water system

No. of observation	**Volume of water added (mL)**	**% (w/w) of phenol**	**Miscibility temperature (ºC)**		**Mean temperature(ºC)**
			Disappearance of turbidity	**Reappearance of turbidity**	

(4) Table-2: Determination of CST for Phenol-aq. NaCl solution system

No.of observation	Volume of 0.1(N) NaCl added (mL)	%w/w of phenol	Miscibility temperature(°C)		Mean temperature (°C)
			Disappearance of turbidity	Reappearance of turbidity	

Calculation & Graph plotting:

% (w/w) of phenol = Weight of Phenol/ Weight of phenol+(volume of liquid added× density of liquid)

Plot mean miscibility temperature **(°C)** as ordinate against concentration of phenol (percentage by weight) as abscissa for both the system. From the maxima of the curve find out critical solution temperatures (of phenol-water and phenol-aq.NaCl solution system) and corresponding compositions.

Precautions and Suggestions:

1) The temperature of the solution should be increased or decreased very slowly.
2) The mixture of phenol and experimental liquid should be continuously and uniformly stirred.
3) The stirrer should not touch the bottom of the tube.
4) Care should be taken while handling phenol.

Experiment 4: pH-metric titration of acid (mono- and di-basic) against strong base.

Theory:

pH of an aqueous solution can be measured using glass electrode. It is a reversible electrode like Ag-AgCl immersed in a solution of fixed pH within a thin walled bulb of a

special quality of glass which is immersed in a solution of unknown ph. The glass electrode is actually an ion selective membrane electrode reversible with respect to hydrogen ion (H^+ ion). When this electrode is coupled with a saturated calomel electrode an electrochemical cells is formed as follows:

Ag/ AgCl (s) / 0.1 (M)HCl (aq)/ Glass/ solution of unknown pH/ Saturated Calomel electrode

Overall electrode potential (EMF) of the cell (E_{Cell}) is given by,

$E_{Cell} = E_R - E_L = E_{SCE} - E_g = E_{SCE} - E_g^0 + \frac{2.303RT}{F}$ pH

Or, pH = $(E_{cell} - E_{SCE} + E_g^0) \frac{F}{2.303RT}$

From the measurement of EMF of the electrochemical cell obtained on coupling glass electrode with a reference calomel electrode the pH of different solutions can be compared. Once this cell (known as pH meter) is calibrated by means of solutions of known pH (buffer solutions), it can be conveniently used for measurement of pH of any unknown solution.

Dissociation constant of a weak acid can be determined pH- metrically by titrating the weak acid with a strong base. Ionization of a weak monobasic acid (HA) in aqueous solution may be represented as $HA \rightleftharpoons H^+ + A^-$

At equilibrium ionization constant (k_a) is given by $k_a = \frac{a_{H^+} a_{A^-}}{a_{HA}}$

Where 'a' represents activity of the respective species . In dilute solution (when activity coefficients approach unity) activity may be replaced by molar concentration. Consequently k_a may be expressed as $K_a = \frac{[H^+][A^-]}{[HA]}$

When a strong base is added to a weak acid a buffer solution is formed, the pH of which is given by the Henderson's equation (valid within the pH range 4 to 10):

$$pH = pk_a + \log \frac{[Salt]}{[Acid]}$$

At the half neutralization point [Salt] = [Acid] and pk_a = pH at the half neutralization point.

A pH metric titration curve may be obtained by plotting pH of the acid solution vs number of drops of strong base added. From the pH of the solution corresponding to the half neutralization point pk_a and hence k_a (for weak monobasic acid) can be determined.

For weak dibasic acid like oxalic or succinic acid (H_2A), the ionization equilibrium can be written as,

$H_2A \rightleftharpoons HA^- + H^+$, dissociation constant K_1

$HA^- \rightleftharpoons H^+ + A^{2-}$, dissociation constant K_2

Beyond the half neutralization point the system behaves like a buffer consisting of HA^- and A^{2-} .

The pH of this buffer solution is given by

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

At ¾ th of the equivalence point $[A^{2-}]$ = [HA^-] and pk_2 = pH at ¾ th of the equivalence point.

A pH metric titration curve may be obtained by plotting pH of the acid solution vs number of drops of strong base added. From the pH of the solution corresponding to the ¾ th of the equivalence point pk_2 and hence K_2 (for weak dibasic acid) can be determined.

Apparatus required:

1) 100ml vol. flask -1
2) 100ml beaker -1
3) 250ml glass bottle -3
4) Burette -1
5) Pipette 10ml -1

Chemicals required:

NaOH, Oxalic acid, succinic acid, acetic acid.

Procedure:

1) Prepare 100ml of ~ (N/10) oxalic acid solution by accurate weighing.
2) Prepare 250ml ~ (N/10) acetic acid and succinic acid each.
3) Prepare approximately 100ml of ~ (N/2) NaOH solution.
4) Take the NaOH solution in a burette. Determine the volume of 50drops and calculate the volume of one drop.
5) Standardize the pH- meter by alternately dipping the glass- calomel electrode assembly in pH = 4.0 and pH = 7.0 buffer solutions.
6) Standardize the (N/2) NaOH solution in the following way.
   Pipette out 10ml of the prepared oxalic acid solution in a100ml beaker, add sufficient distilled water to cover the electrode. Add (N/2) NaOH solution from a burette, two drops at a time till the pH crosses the value 5.0 and subsequently one drop at a time and measure the pH each time, till the end point is reached. Final pH should not exceed 10.5.
7) Pipette out 10ml of the prepared acetic acid solution in a 100ml beaker. Repeat the step (6) with this solution .
8) Pipette out 10ml of the prepared succinic acid solution in a 100ml beaker. Repeat the step (6) with this solution.
9) Plot the pH versus number of drops of alkali added for the prepared oxalic acid, acetic acid and succinic acid solution in separate graph papers.
10) From the corresponding titration curves find (a) concentration of NaOH solution and pk_2 of oxalic acid, (b) concentration and pk_a of acetic acid and (c) concentration and pk_2 of succinic acid.

Experimental result:

1) Room temperature.

2) Preparation of 100ml standard (N/10) oxalic acid solution.
3) Preparation of 250ml (N/10) acetic acid.
4) Preparation of 250ml (N/10) succinic acid solution.
5) Preparation of 100ml of~ (N/2) NaOH solution.
6) 50 drops of NaOH solution = ……..ml NaOH.
7) pH metric titration of (N/10) oxalic acid vs~ (N/2) NaOH solution:

Volume of (N/10) oxalic acid solution	Number of drops of NaOH solution added	Total number of drops of NaOH solution added	pH
10ml			

8) pH metric titration of (N/10) acetic acid vs ~ (N/2)NaOH solution:

Volume of (N/10) acetic acid solution	Number of drops of NaOH solution added	Total number of drops of NaOH solution added	pH
10ml			

9) pH metric titration of (N/10) succinic acid vs ~(N/2) NaOH solution:

Volume of (N/10) succinic acid solution	Number of drops of NaOH solution added	Total number of drops of NaOH solution added	pH
10ml			

Graph plotting:

Plot the pH versus number of drops of alkali added for the prepared oxalic acid, acetic acid and succinic acid solution in separate graph papers.

Calculation:

From the corresponding titration curves for acetic acid, oxalic acid and succinic acid respectively at equivalence point,

…….. drops NaOH solution ≡ …….ml NaOH = V_{NaOH}

Therefore,

Strength of NaOH solution, $(S_{NaOH}) = (V_{oxalic} \times S_{oxalic})/ V_{NaOH}$

Strength of succinic acid, $(S_{succinic}) = (V_{NaOH} \times S_{NaOH})/ V_{succinic}$

Strength of acetic acid, $(S_{acetic}) = (V_{NaOH} \times S_{NaOH})/ (V_{acetic})$

From the titration curve for acetic acid, pH at half equivalence point, $(pH)_{1/2} = pK_a$

From the titration curve for oxalic and succinic acid, pH at ¾ th of the equivalence point, $(pH)_{3/4} = pk_2$

Experiment 5: Determination of solubility of sparingly soluble salt in water, in electrolyte with common ions and in neutral electrolyte (using common indicator)

Theory:

Solubility of a substance in a solvent is defined as the number of grams of the solute required to saturate 100 gm of the solvent at a given temperature.

When excess of an electrolyte A_xB_y is shaken with water (solvent) a saturated solution of the electrolyte will ultimately be formed and the constituent A^{y+} and B^{x-} of the dissolved electrolyte will then be in equilibrium with the pure electrolyte that forms different phase (solid, liquid or gas).

$$A_xB_y\,(\text{pure}) \rightleftharpoons A_xB_y\,(\text{in solution}) \rightleftharpoons x\,A^{y+} + y\,B^{x-}$$

Application of thermodynamic principle on this equilibrium leads to the following relation between the chemical potential μ of pure A_xB_y and the chemical potential $\mu_A{}^{y+}$ and $\mu_B{}^{x-}$ of +ve and –ve ions respectively.

$$\mu = x\,\mu_A{}^{y+} + y\,\mu_B{}^{x-} = x(\mu^{*Ay+} + RT\ln a_A{}^{y+} + y(\mu^{*Bx-} + RT\ln a_B{}^{x-})$$

Where μ^{*Ay+} and μ^{*Bx-} are constants at a given temperature (and pressure). Since μ is constant (being chemical potential of pure substance) under the same condition. It follows that

$$a^x{}_A{}^{y+}\, a^y{}_B{}^{x-} = K_{th}\ (\text{constant}) \qquad \ldots\ldots(1)$$

This constant K_{th} is called the activity (thermodynamics) solubility product of the electrolyte which is the product of activities of the constituent ions where each activity term is raised to the power same as its stoichiometric coefficient at a given temperature.

For a solution of sparingly soluble electrolyte when ionic strength is low activity 'a' may be replaced by molar concentration 'c'. Then equation (1) becomes

$$c^x{}_A{}^{y+}\, c^y{}_B{}^{x+} = K_{sp}\ (\text{constant})$$

K_{sp} is called the (concentration) solubility product of the electrolyte which represents the greatest possible product of the molar concentration of the constituent ions where each concentration term is raised to the power same as its stoichiometric coefficient at agiven temperature.

Effect of ionic strength on solubility:

In case of electrolyte A_xB_y,

$K_{th} = a^x_A{}^{y+}\ a^y_B{}^{x-} = c^x_A{}^{y+}\ c^y_B{}^{x+}\ \gamma^x_A{}^{y+}\ \gamma^y_B{}^{x+} = K_{sp}\ \gamma^{x+y}$, where the terms have their usual significance. In solution of low ionic strength (1), the mean ionic activity co-efficient (γ_+) is given according to Debye-Huckel limiting law,

$\log(\gamma_+) = -0.51 Z_A{}^{y+} Z_B{}^{x-} \sqrt{1}$ at 25ºC foe aqueous solution.

On addition of an electrolyte to saturated solution of another electrolyte the solubility of the later may increase or decrease depending on the condition as below :

1) If the added electrolyte has no ion common with the electrolyte under discussion then the addition of former will result in increase of K_{sp} and hence solubility , due to decrease in γ_+ resulting from increase in 'I'.
2) If an electrolyte (having a common ion) is added to the saturated solution of the given electrolyte, the solubility of the given electrolyte will decrease (provided there is no complex formation). But the effect of increased ionic strength will be to increase the solubility. However, at low ionic effect the common ion effect is observed predominately.

   The solubility of sparingly soluble electrolyte A_xB_y in 'm' molar solution of an electrolyte MB (which completely dissociates) can be calculated by the following relation from the knowledge of solubility product K_{sp}

   $K_{sp} = (xS_0)^x\ (yS_0)^y$,in water
   $= (xS)^x\ (yS_0)^y$,in water
   $(xS)^x(yS+m)^y$, in 'm' molar solution of MB

   Where S_0 and S denote the solubility in moles/lit of electrolyte in water and 'm' molar solution of MB repectivity.

Apparatus required:

1) 100 mL volumetric flask-3
2) 500 mL glass bottle -1
3) 125 mL stoppered glass bottle-3
4) One burette
5) One 10 mL pipette
6) Funnel-1
7) 250 mL conical flask
8) Dry beaker/100 mL conical flask-3

Chemicals required: KHTa solid, Oxalic acid, KCl, $NaNO_3$, Phenolphthalein

Procedure:

1) Prepare 100 mL (N/10) oxalic acid solution by accurate weighing.

2) Prepare 100 mL~N/20) KCl solution and 100 mL~(N/20) $NaNO_3$ solution by accurate weighing.
3) Prepare 250 mL approximately 0.04(N) NaOH solution and standardize it against the oxalic acid solution using 10 mL aliquot of acid and phenolphthalein as indicator.
4) In three clean and dry 125 stoppered glass bottles take about 1.0 gm each of the supplied bottle add~50 mL of distilled water, in second bottle add~50 mL of prepared electrolyte(KCl) solution and third bottle add~50 mL of prepared electrolyte ($NaNO_3$) solution. Shake the bottles till equilibrium is reached and a saturated solution is obtained. Check that some solid still remains undissolved (if necessary add some more solid and shake).
5) Dry filter the solutions, reject the first few mL of the filters and then collect the residual filtrates in three separate clean dry containers. Take 10 mL of the filters (separately) as aliquot and titrate against the standardization NaOH solution. Perform the titration at least twice in each case. Use phenolphthalein as indicator.
6) Determination the solubility and solubility product of potassium hydrogen tartrate in water and solubility of potassium hydrogen tartarate in the prepared electrolyte solution (KCl & $NaNO_3$).

Experimental result:

1) Room temperature:
2) Preparation of 100 mL 0.1(N) Oxalic acid:
3) Preparation of 100 mL 0.05(N) KCl solution and 100 mL 0.05(N) solutions:
4) Preparation of 250 mL approximately 0.04(N) NaOH solution:
5) **Standardisation of NaOH solution against standard oxalic acid solution:**

Volume of Oxalic acid (mL)	**Burette reading**		**Volume of NaOH used (mL)**	**Average volume of NaOH (mL)**
	Initial(mL)	**Final(mL)**		
10				
10				

Strength of NaOH solution:

6) **Preparation of different sets:**

Bottle NO.	**Volume of water (mL)**	**Volume of prepared electrolyte (mL)**	**Amount of KHTa added (g)**
Set 1	~50	**0**	-1
Set 2	0	~50	-1
Set 3	0	**~50 (**$NaNO_3$)	-1

7) Titration of HTa-from different sets:

Bottle no	Volume of filtrate (mL)	Burette reading		Volume of NaOH used (mL)	Average volume of NaOH (mL)	Conc. Of HTa^-
		Initial (mL)	Final (mL)			
Set -1	10					
	10					
Set-2	10					
	10					
Set-3	10					
	10					

8) Calculation of the solubility of salt (mol/litre) in aqueous solution and in the prepared electrolyte solutions.
9) Calculation of the solubility product [no unit or $(g\text{-ion/L})^2$ in water.

Precautions and suggestions:

1) At first prepare the sets and occasionally shake them by swiriling motion (at least for 45 minutes). Do other tasks as per procedure in between shaking.
2) If the clean stoppered bottle are not dry, rinse them with small amount of electrolyte solutions and then prepare the sets.
3) Check that some solid still remains undissolved in the prepared sets (if necessary add some more solid and shake).

Experiment 6: Study of kinetics of acid-catalyzed hydrolysis of methyl acetate:

Theory:

The acid catalysed hydrolysis reaction of ester can be represented as

$$R_1COOR_2 + H_2O + H^+ \rightleftarrows R_1COOH + R_2OH$$

The rate equation is represented as

$-\frac{d[R_1COOR_2]}{dt}$ = $k[R_1COOR_2][H^+][H_2O]$

= $k_1[R_1COOR_2]$, where $k_1=k[H^+][H_2O]$ = constant, (in large excess of water,$[H_2O]$ remains constant and H^+ being the catalyst $[H^+]$ is constant)

Therefore the reaction becomes first order w.r.t ester. Integration of this equation with the boundary conditions, when t= 0, $[R_1COOR_2] = C_0$ and at time t, $[R_1COOR_2] = C$, gives

$$K_1=(2.303/t)\log (C_0/C)$$

The progress of the catalysed reaction may be studied by withdrawing measured volume of aliquot from the reaction mixture at different intervals of time and titrating with standard alkali solution using phenolphthalein indicator. The volume of alkali required at any instant is equivalent to be the sum of weak acid (produced as a result of hydrolysis) and the acid used as catalyst (a constant quantity).

If V_0, V_n and V_∞ be the volumes of alkali required for the same volume of aliquot at the beginning, at time t= t_n and at the end of the reaction (at infinite time) respectively then,

$C_0 \propto (V_\infty - V_0)$ and $C \propto (V_\infty - V_n)$

Then, $k_1=\frac{2.303}{t_n} log \frac{(V\infty - V0)}{(V\infty - Vn)}$

To avoid the measurement of V_0 the equation may be represented in the form

$\Delta t_n = t_n - t_1 = \frac{2.303}{k_1} log \frac{(V\infty - V1)}{(V\infty - Vn)}$

Where V_n and V_1 are the volumes of alkali required at times t_n and t_1 respectively.

Plot of $log \frac{(V\infty - V1)}{(V\infty - Vn)}$ vs Δt_n will give a straight line passing through the origin and the slope k_1 may be determined by

$$K_1=\text{slope}\times 2.303$$

Apparatus required:

1) 100 mL dry conical flask-1
2) 500 mL bottle for NaOH.
3) 2 mL pipette; 5 mL pipette-1 each
4) 250 mL conical flask-5
5) Sufficient ice cold water; water bath
6) **Stop watch**

Chemicals required: Methyl acetate, NaOH, and Phenolphthalein

Procedure:

1) Prepare 250 mL of approximately 0.1(N) NaOH solution.

2) Prepare 100 mL 1(N) HCl solution
3) Pipette out 50 mL of prepared HCl solution (catalyst solution) in a 100 mL dry conical flask, add 5 mL of ester using a pipette. Start the stop watch at the time of half discharge. Mix the solution thoroughly by swirling motion.
4) At 5-7 minutes intervals take 2 mL aliquot and add to 50 mL ice cold water taken in a 250 mL conical flask. Note the time of half discharge. Titrate rapidly against the prepared~0.1(N) NaOH solution taken in a burette, using phenolphthalein as indicator. Take at least 6 readings.
5) The remaining solution is heated at about 60ºC in a water bath~for 40 minutes with an air condenser fitted in the mouth of conical flask. The solution is allowed to cool to room temperature. Pipette out 2mL of it in 50 mL water taken in a 250 mL conical flask and titrate with~0.1(N) NaOH solution; using phenolphthalein as indicator. The titre value correspond to V∞.
6) Plot a graph of $log\frac{(V\infty - V1)}{(V\infty - Vn)}$ vs Δt_n and draw the best fit straight line passing through the origin.
7) Calculate the value of 'k_1' from the slop of the graph.

Experimental result:

1) Room temperature
2) Preparation of 250 mL~0.1(N) NaOH solution: Dissolve 1 g NaOH in 250 mL deionized water.
3) Preparation of 100 mL 1(N) HCl solution: Dissolve~9mL conc. HCl in 91 mL deionized water
4) Recording of data for ester hydrolysis:

Time(t)	Time(t_n)in sec	$\Delta t_n = t_n - t_1$	Volume of NaOH(V_n mL)	($V_\infty - V_1$) mL	($V_\infty - V_n$)mL	$log\frac{(V\infty - V1)}{(V\infty - Vn)}$

5) Determination of V_∞:
V_∞ = Volume of NaOH required to standardize 2 mL reaction mixture after heating at about 60ºC in a water bath.

6) Plotting of graph:

$log\frac{(V\infty - V1)}{(V\infty - Vn)}$						
Δt_n(Sec)						

Calculation: Observed rate constant, k_1=slope×2.303

Conclusion: Therefore observed rate constant for the acid catalyzed hydrolysis of methyl acetate at …..ºC is…..sec^{-1}.

SEC2: Chemistry of Cosmetics and Perfumes Lab

Experiment 1: Preparation of talcum powder

Introduction:

One important category of skin care preparations is powders. Widely used for face and body care, not only by women but also by men. There are body powders (dusting /talcum powders), Face powders and compacts, medicated powders for prickly heat or preventing microbial growth or skin.

Talcum powder is one of the most popular beauty care product used by men and women including infant to keep the skin dry, to suppress the bad (sweat) odour and to feel fresh. Three types of talcum powders are generally found in the market for men, for women and body powder.

All talcum powder is enriched with nice fragrances which make each and every end used to stay active throughout his/her working day, or during travel or any other accession. Talcum powder helps in giving a real glow to skin and relieves skin from nice fragrance and keeps entire day active and fresh. It gives relief to irritate and skin and prevents chafing. Talcum powder is used on an instant to keep skin softer and keeping them cheerful and happier.

Characteristics of good powder:

- The powder must have good covering powder and so hide skin blemishes .
- It must adhere perfectly to the skin and not blow off easily .
- It must not be completely dissipated in a few minutes .
- Powder must be absorbent .
- There must be sufficient slip to enable the powder to spread or the skin .

Properties of Raw Material for powder :

- The row material to be used for manufacturing powder should be of good quality.
- Material should not be hard. If the materials are crystals in nature they must not have any sharp edges or points . These can damage the skin .
- The material should be non –irritating and non toxic to the skin .
- The material must be chemically neutral and should not interact with each other .

Ingredients of Talcum powder :

- **Covering powder :** The ability to mask skin imperfections such as skin shine , enlarged pores and minor blemishes .
- **Slip :** The character of spreading over the skin without dragging and giving the characteristic of smooth feeling .
- **Absorbency :** The ability to absorb skin perspirations and oily secretion without showing the effect of such absorption .
- **Bloom :** The ability to impart a velvety , peach –link finish to the face skin .

- **Colour :** To impart a colour effect according to the need .
- **Perfume:** To produce a pleasant odour. Very small amount of perfume is added the effect .
- Other ingredients.

  Talcum powder consists mainly of Talc mixed with other ingredients like boric acid for antiseptic properties, colour and perfume .

Ingredient	Category	Use
Talc	Base / Mineral	Naturally occurring mineral added in safe amount .
Mica	Covering agent	It helps the powder to study on the skin louger .
Koolin	Slip / Adsorbent	Enhance coverage while reducing the sheen provided by talc .
Magnesium Stearate	Adhesive	Improves the consistency of face powders , ensuring a smooth application .
Calcium Carbonate	Adsorbent	Absorbs moisture to minimize oiliness and create a matte finish.
Inorganic and organic pigments triclasan .	Colorant perfumes	Added to the formula to create the desired tint. Enhance the intrinsic appeal.

- **Procedure :**

Sl.No.	Ingredients	%(W/W)	%(W/W)	Spoon measuring
1.	Talc	79	19	7 Table spoon
2.	Becipitated chalk	15	–	–
3.	Boric Acid	3	5	½ Table spoon
4.	Perfume	1	1	According to preference
5.	Magnesium sterate	**2**	–	–

6.	Calcium carbonate	_	60	3 Table spoon
7.	Rice starch	_	13	_
8.	Kaolin clay	_	2	3-4 Table spoon

Mix all the ingredients one by one as per the measurements . Add 5-6 drops of essential for a good results . Now mix the ingredients and transfer to a airtight box . Rest for after mixing the Hydrated magnesium silicate (Tale) with perfume .

Experiment 2: Preparation of shampoo

- **Introduction :**

A Shampoo is a preparation of a surfactant (i.e. surface active material) in a suitable from –liquid ,solid or powder –which when used under the specified conditions will remove surface grease , dirt and skin debris from the hair shaft and scalp without adversely affecting the user.

- **Formulation Parameters**

Shampoo: i. Viscous liquids
ii. clear or opaque
iii. containing 20-30% solids
iv. viscosities 500-1500 centipoise

Sl.No.	Ingredients	For 500 ml of shampoo preparation volume measurement(ml)	Use

1.	S.L.E.S (sodium Lauryl Ether Sulphate)	(300ml)	Surfactant
2.	DM/RO water	(60ml)	Reduce irritates by diluting the cleaning agents . Add natural shim and smoothness to hair and reduce irritation .
3.	Aloe- vera gel	(60ml)	
4.	Glycerine	(40ml)	
5.	Vitamin –E oil	(10ml)	For softness
6.	Tea-tree oil	(2ml)	Antibacterial
7.	Essential oil (Fragrance)	(10ml)	For fragrance
8.	Any colour (wica powder)	According to need	For colour effect
9.	Pearl powder	20 gms (by weight measurement)	For shining effect

Add all the ingredients one by one in a clean 500ml beaker , mix all of them and after transfer it to a clean empty 500ml bottle . Thus our 500ml shampoo is prepared .

Experiment 3: Preparation of Enamels

Introduction :

Enamel paint can be defined as the oil based paint can be defined as the oil based point that is used when a highly glossy finish is required .It consists of white lead , zinc white , resins and other petroleum products . If is slow drying paint as it dries very slowly . It is hard in nature and provides a glossy and opaque finish to the surface where it is applied . It also offers oxcellent durability and stain resisting properties . It may also be water –based .

Composition of Enamel paint :

1. Base :

White lead ,or read lead or zinc oxide ,or iron oxide ,or titanium white , or aluminium powder , or lithophone may be used as the base.

2. Vehicle / Binder:

Mostly linseed oil ,or alkyd resins , or acrylic resin ,or empty resins are used as the vehicle .

3. Extender / Inert filler :

Usually , the coloured particles are used as the extenders .

4.Solvent / Thinner :

Mostly , the varnish or white spirit is used as the solvent or Thinner.

5.Colouring pigments :

The fine powder of mineral colour pigments is used as the colouring pigments .

6. Additives:

Various drying or pigments such as lead ,copper , cobalt , manganese , zirconium etc may be usd as the additives .

- ## Preparation of Enamel :

  Paint is prepared according to the manufacture’s manual by adding a suitable amount of thinner.

	Guide formulation
Binder	
Mowilith LDM 1871	12.59
Solvent	
Water	28.23
Additives	
Lopon 895	0.31
Calgon N	0.73
Natrosol 250 HR	0.31
Schwego Foam 6351	0.31
Silires BS 333with and without	(1.05)
Acrysol RM8	0.24
Pigment and Fillers	
Omyacarb 5 Gll	27.02
Omyacarb Extra	7.57
SoCal P2	3.24
Knonoj 2300	10.81
Different type of Talc	7.57
Total	**100.00**
PVC(pigment volume concentration)	70

Mix all these ingredients with base. Transfer to thinner tank. Then do a quality test .Now, the paint (enamel) is ready to

Experiment 4: Preparation of Hair Remover

Introduction:

Hair removers , or depilatories , are products designed to chemically or physically remove undesirable hair from areas on the body . Hair removers are made by mixing together the appropriate row materials in large . Stainless steel tanks and then filling them into individual packages . In use for thousands of years , they continue to be an important part of many people's everyday hygiene . Currently , New hair removers are being investigated which are less irritating ,more effective ,and longer lasting .

Raw Materials :

There are many different materials that have been used in hair remover formals. Some of these materials are responsible for the hair removing properties of the product while others are needed to improve the products aesthetics .

1. Calcium Thioglycollate trihydrate **5-7**
2. Calcium Carbonate 15-18
3. Mineral oil 4-6
4. Cetyl alcohol 0.3
5. Sodium Lauryl Sulphate (powder or needed) 0.3-0.7
6. Glycerin 3-5
7. Purification water rest to complete raion 100
8. Perfume
9. Calculation Hydroxide sufficient to adjust P^H
10. Colour

Procedure :

1. Minerals and cetyl alcohol mix both and heat 70-80^0 to melt .

2. S.L.S (sodium lauryl sulphate) and some water mix another vessel (heat to dilute). After that mix(1&2) products and make a cream paste.

3. Glycerine +Calcium Thioglycollate and calcium carbonate mix into a paste from with sufficient water. Add this mixture paste in the main mixture paste (1&2).

4. In another vessel mix the calcium . Hydroxide in purified water with stirring uniformly .

Add this mixture to the main mixture of (1&2&3) .Adjust P^H of cream to around 11.5 -12.5 and mix at 15to 20 minutes. Fill the empty containers with the hair remover cream prepared.

N.B: D_0 mix all the ingredients in a stainless steel.

Experiment 5: Preparation of Face Cream

Introduction :

Face creams are semi-solids emulsions which contain mixture of oil and water . Their consistency varies between liquids and solids . Salve (medical ointment for soothing purpose)and urgent (soothing product) preparation in earlier days led to the development of cleansing and cold creams . A face cream is essential for every age .Face cream also nourish the skin and keep it healthy looking .with the help of additives such as emulsifying agent and newer technique ,the preparation of creams has become easy .

Properties of Face Cream :

- They are easy to apply
- They spread easily on the skin
- They are pleasant in appearance
- They cause less irrilation to the skin
- They should well or liquefy
- They should produce flushing action or skin and it's pore openings .
- They should form an emollient film on the skin after application.
- They should not make skin dry which happens in case , when the skin is washed with water and soap.
- They also help in softening ,lubricating and protecting skin apart from cleansing purposes.

Ingredients and its composition :

1. Work powder	(50gms)
2.DM/RO water	(150ml)
3.Glycerine (moisture lack)	(2-5ml)
4. Preservative (Tocopherol acetate)	(2-5ml)
5. Vitamin –E oil (anti aging)	(2-5ml)
6. Perfume (Fragrance)	(2-5ml)
7.Rose water	(2-5ml)

Procedure :

At first , heat up the work powder with some water , make a paste and then mix rest of all the ingredients of mentioned amount . Thoughroly mix up,fill the cream consistency appears . Transfer to a clean empty container (air tight) . Store it, .Thus,our face cream is being prepared .

Experiment 6: Preparation of nail polish and nail remover:

Introduction:

Nail lacqures / paints are viscous preparation intended to decorate rails for fingers and toes .

Nail removers are defined as the mixture of solvents containing small amounts of fall intendent to remove the nail enamel .

Ideal Characteristics :

- **Nail polish :**
  - It should have proper viscosity wetting and flow properties .
  - It should have uniform colour .
  - It should have good and good adhesive properties .
  - It should have sufficient flexibility so that it does not crack or become brittle.
  - It should be able to maintain the above mentioned properties for a reasonable time (about 1 weak).
- **Nail Remover:**

An ideal Nail paint Remover should have the following characteristics :

- It should not be too volatile to evaporate during application .
- It should not be non-irritating to surrounding skin.
- It should not leave the nails fatty or sticky .
- It should not have strong degreasing effect to leave nails brittle .
- It should not have unpleasant and obstructive odor.

Manufacture:

Nail lacquers / polish / paints :

Add 75% of the solvent and whole of the diluent in a mixed .

↓

Mix well with agitation

↓

Nitrocellulose is then added with stirrer on

↓

Solvent is added

↓

Plasticizer is added

↓

Resin is added

↓

Mixing is continued for several hours until solution of all

Ingredients is complete.

↓

Clear lacquer is formed

↓

Passed through filter

↓

Centrifuged.

↓

Pigmented chips or concentrated tenors are added

and mixing is continued.

↓

Nail liquor product is formed

Formulation of Nail point / lacquer:

Ingredients	% weight
Nitrocellulose (film former)	11.0
Butyl acetate (solvent)	24.0
Toluene (solvent)	15.0
Formaldehyde resin (to make film adhere)	12.0
Camphor (plasticizer)	0.5
Titanium di-oxide (colourant)	3.0
Ethyl acetate (solvent)	27.0
Di-Acetone (solvent)	0.5
Di-butyl phthalate (plasticizer)	0.5
Stearyl konium hectorile (Thickening Agent)	2.0
Total	100

Nail paint removers:

Formula :

Ingredients	**%**

Amyl Acetate	**60**
Ethyl Acetate	**40**
Acetone	**10**
Thinner (Butylacetate + Acetone	

Mixing all the ingredients in a clean coutainer and dip a cotton pad and apply it on nail paint. It will easily get away. Thus, the nail point remover is ready to stored and use.