A LABORATORY MANUAL

FOR

SEMESTER I

CHEMISTRY (HONORS) STUDENTS

Edited by

DEPARTMENT OF CHEMISTRY

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1. Titrimetric Analysis

a.Experiment: Calibration and use of common laboratory apparatus.

Theory: There are various apparatus which are commonly used in laboratory. These include burettes, pipettes, graduated cylinders etc. The accuracy of a titrimetric analysis depends on the accuracy with which the volumes of the solutions are measured that depends on the accuracy of the apparatus used.Therefore calibration is necessary to find out the percentage error.

Procedure: For calibration, a known volume of water is measured with the apparatus to be calibrated and put this water into a dry previously weighed conical flask. The conical flask with water is weighed and also the temperature of the water is noted. Then from the difference of the two weights, the weight of the water delivered is calculated. The process is repeated at least three times. Then the error is calculated from the observed data. With this procedure, pipettes, burettes, conical flasks can be calibrated.

Calculation:

Serial No.	Weight of the flask (W$_1$ g)	Weight of the flask + water (W$_2$ g)	Weight of the known volume of water (W$_2$-W$_1$) g	Correct volume (W$_2$-W$_1$)/Density	Error

b.Experiment: Preparation of solutions of different Molarity/Normality of titrants.

Theory: The concentration of standard solutions can be expressed in terms of molarity, normality and percentage.

Molarity(M): Molarity is defined as the moles of a solute dissolved in one litre of a solvent.

Molarity(M) = Number of moles of solute x 1000/ Volume of solution in ml

Normality(N): Normality is defined as the number of gram equivalents of a solute dissolved in one litre of a solvent.

Normality(N) = Number of gram equivalents x 1000/ Volume of solution in ml

(i)Oxalic acid ($H_2C_2O_4.2H_2O$): Mol. wt. 126; Eq. wt. 63

For 1M solution, 126g of oxalic acid should be dissolved in one litre and for 1N solution, 63g should be dissolved in one litre. Likewise, for a N/20 250 ml solution, the amount of oxalic acid to be dissolved is: 63/20 x 250/1000 = 0.7875g. Let an amount of 0.788g weighed accurately and dissolved in 250ml of distilled water, the normality of the solution can be calculated as, N/20 x 0.788/0.7875.

(ii)Sodium carbonate (Na_2CO_3): Mol. wt. 106; Eq. wt. 53

For 1M solution, 106g of anhydrous sodium carbonate should be dissolved in one litre and for 1N solution, 53g should be dissolved in one litre. Similarly, to prepare a N/20 250 ml solution, the amount of anhydrous sodium carbonate required is: 53/20 x 250/1000 = 0.6625g. Therefore, to get a N/20 solution, 0.6625g of anhydrous sodium carbonate is to be dissolved in 250 ml of distilled water.

## 2. Acid-Base Titrations

a.Experiment: Estimation of carbonate and hydroxide present together in a mixture.

Theory: If a mixture of sodium carbonate and sodium hydroxide containing phenolphthalein as the indicator is titrated against a standard acid solution, the pink colour of the indicator gets discharged when whole of sodium hydroxide and half of the carbonate present in the solution (upto the bicarbonate stage) get neutralized.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \longrightarrow NaCl + NaHCO_3 \qquad \text{………. (i)}$$

To the above neutralized solution, 2-3 drops of methyl orange indicator are added followed by a further quantity of the acid till pink colour is obtained. This quantity of the acid added corresponds to the quantity required to neutralize the remaining half of the carbonate means neutralization of the bicarbonate.

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2 \qquad \text{…………(ii)}$$
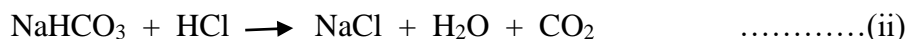
The amount of acid required for reactions (i) and (ii) must be the same as one molecule of sodium bicarbonate is produced from one molecule of sodium carbonate.

Procedure: It involves the following steps:

(i)Standardisation of HCl solution using standard Na_2CO_3 solution: 20ml of 0.05M Na_2CO_3 solution is pipetted out into a conical flask. Two drops of methyl orange indicator are added into it. This solution is titrated with HCl solution. At the end point, the colour changes from golden yellow to orange red. The process is repeated to get three concordant readings.

(ii)Estimation of Na_2CO_3 and NaOH: 20 ml of the sample solution is pipetted out into a conical flask. To it, 2-3 drops of phenolphthalein is added as the indicator. Then it is titrated with the standardized HCl till the pink colour of the solution gets discharged. This is the first end point.

To the same solution in the conical flask, 2-3 drops of methyl orange indicator is added and titrated again with the standardized HCl solution from the burette till the yellow colour of the solution changes to pink. This is the second end point. Titrations are repeated to get three concordant readings.

Calculations: Let 20 ml of the mixture solution requires V_1 ml of the 0.05M HCl using phenolphthalein as indicator, so this neutralizes entire NaOH and one half of the carbonate present in the mixture. Let the additional volume of 0.05M HCl required to neutralize the remaining half of the carbonate as indicated by methyl orange be V_2 ml.

Therefore, the volume of the acid required to neutralize carbonate completely is $2V_2$ ml and the volume of the acid required to neutralize NaOH is (V_2-V_1) ml.

(i)Calculation of strength of sodium carbonate:

Na_2CO_3 present in 20 ml of mixture solution = $2V_2$ ml of 0.05M HCl

$20 \times M_{Na2CO3} = 2V_2 \times 0.05M$

(ii)Calculation of strength of sodium hydroxide:

NaOH present in the mixture solution = (V_2-V_1) ml of 0.05M HCl

$20 \times M_{NaOH} = (V_2-V_1) \times 0.05M$

The amount of Na_2CO_3 in the mixture = M_{Na2CO3} x 106 g

The amount of NaOH in the mixture = M_{NaOH} x 40 g

b.Experiment: Estimation of carbonate and bicarbonate present together in a mixture.

Theory: This experiment is based on the selective use of indicators. When methyl orange is used as indicator, the volume of 0.1N HCl used in the titration neutralizes both sodium carbonate and bicarbonate completely. Let the volume of the acid be V_1 ml.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$
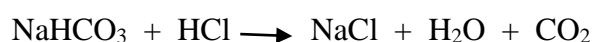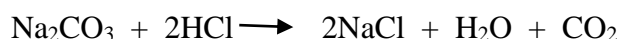
When phenolphthalein is used as indicator, the volume of 0.1N HCl used in the titration neutralizes only half of the sodium carbonate. Let the volume of the acid be V_2 ml.

$$Na_2CO_3 + HCl \longrightarrow NaCl + NaHCO_3$$
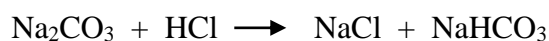
Therefore, the volume of acid used up for complete neutralization of sodium carbonate will be $2V_2$ ml and the volume of acid for neutralization of sodium bicarbonate will be (V_1-2V_2) ml.

Procedure: It involves the following steps:

(i)Standardisation of HCl solution using standard Na_2CO_3 solution: 20ml of 0.1N Na_2CO_3 solution is pipetted out into a conical flask. Two drops of methyl orange indicator are added into it. This solution is titrated with HCl solution. At the end point, the colour changes from golden yellow to orange red. The process is repeated to get three concordant readings.

(ii)Titration with methyl orange as indicator: 20 ml of the sample solution is pipetted out into a conical flask. To it, 2-3 drops of methyl orange indicator is added. Then it is titrated with the standardized HCl solution till the pink colour of the solution turns pink. The process is repeated to get three concordant readings.

(iii)Titration with phenolphthalein as indicator: 20 ml of the mixture solution is pipetted out into a conical flask. To it, 2-3 drops of phenolphthalein is added as the indicator. Then it is titrated with the standardized HCl solution till the pink colour of the solution becomes colourless. The titration is repeated to get concordant readings.

Calculations:

20 ml of the mixture solution = V_1 ml of 0.1N HCl

Again, 20 ml of the mixture solution = V_2 ml of 0.1N HCl = half of Na_2CO_3 present

So, $2V_2$ ml of 0.1N HCl = Total Na_2CO_3 present in 20 ml of the mixture solution

$2V_2$ x 0.1N = 20 x N_{Na2CO3}

$N_{Na2CO3} = V_2/100$ N

Hence, the amount of Na_2CO_3 present in the mixture = $V_2/100$ x 53 g

Similarly, (V_1-2V_2) ml of 0.1N HCl = Total $NaHCO_3$ present in 20 ml of the mixture solution

(V_1-2V_2) x 0.1N = 20 x N_{NaHCO3}

$N_{NaHCO3} = (V_1-2V_2)/200$ N

Hence, the amount of $NaHCO_3$ present in the mixture = $(V_1-2V_2)/200$ x 84 g

c.Experiment: Estimation of free alkali present in different soaps/detergents.

Theory: Soap is a sodium or potassium salt of various naturally occurring fatty acids. The alkalies present in soap are in the form of hydroxides of sodium or potassium. To estimate free alkali present in a given sample solution, a definite volume of the solution is titrated with standardized HCl solution. The amount of the free alkali present can be calculated from the titre value.

$$\text{Sodium salts of fatty acid } + \text{ H}_2\text{O} \longrightarrow \text{ Fatty acid } + \text{ NaOH}$$

Procedure: 20 ml of the given soap solution is pipetted out in a conical flask and 2-3 drops of phenolphthalein indicator is added to it. The solution is then titrated against standardized HCl solution till the colour of the solution gets discharged. The process is repeated to get concordant readings.

Calculations:

Let, 20 ml of soap solution = V ml of 0.1N HCl

Therefore, the strength of the soap solution = V/20 x 0.1 N

3. Oxidation-Reduction Titrimetry

a.Experiment: Estimation of oxalic acid using standardized KMnO₄ solution.

Theory: $KMnO_4$ is a very strong oxidizing agent. Therefore it can easily oxidize oxalic acid to CO_2 and H_2O. This property of $KMnO_4$ can be utilized for the estimation of oxalic acid in an unknown sample. The reaction involved is given as follows.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

From the above reaction, we have

$$\frac{\text{Molarity of } H_2C_2O_4}{\text{Molarity of } KMnO_4} = \frac{5}{2}$$

Procedure:

(i)Standardisation of KMnO₄ solution: 20 ml of 0.02M oxalic acid solution is pipetted out into a conical flask and to it 20 ml of dilute H_2SO_4 is added. The mixture is heated to about $60\text{-}70^0$ C and then titrated with $KMnO_4$ solution in the burette till the appearance of a permanent pink colour of $KMnO_4$. The process is repeated thrice to get concordant readings.

(ii)Estimation of oxalic acid: 20 ml of the sample oxalic acid solution is pipetted out into a conical flask and to it 20 ml of dilute H_2SO_4 is added. The mixture is heated to about $60\text{-}70^0$ C and then titrated with $KMnO_4$ solution in the burette till the appearance of a permanent pink colour of $KMnO_4$. The process is repeated thrice to get concordant readings.

Calculations:

Volume of sample oxalic acid solution pipetted = 20 ml

Let, the strength of $KMnO_4$ solution = 0.02 M

The volume of $KMnO_4$ consumed = V ml

Therefore,

$$M_{H2C2O4} = \frac{0.02 \times V}{20} \times \frac{5}{2} \text{ M}$$

So, the amount of oxalic acid in the sample solution = $M_{H2C2O4} \times 126$ g

b.Estimation of Fe(II) using standardized KMnO₄ solution.

Theory: As $KMnO_4$ is a very strong oxidizing agent, it can be highly useful for the estimation of ferrous ion by oxidizing it to ferric ion in presence of dilute sulphuric acid. The reaction can be given as follows.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

From the above equation,

$$\frac{\text{Molarity of Fe(II)}}{\text{Molarity of } KMnO_4} = \frac{10}{2}$$

Procedure:

(i)Standardisation of KMnO₄ solution: 20 ml of 0.1M oxalic acid solution is pipetted out into a conical flask and to it, 20 ml of dilute H_2SO_4 is added. The mixture is heated to about $60\text{-}70^0$ C and then titrated with $KMnO_4$ solution in the burette till the appearance of a permanent pink colour of $KMnO_4$. The process is repeated thrice to get concordant readings.

(ii)Estimation of Fe(II): 20 ml of the sample ferrous solution is pipetted out in a conical flask and 20 ml of dilute H_2SO_4 is added to it. Then the solution is titrated with the standardized $KMnO_4$ solution till a permanent pink colour appears. The titration is repeated to get three concordant readings.

Calculations:

Volume of Fe(II) ion pipetted = 20 ml

Let, the strength of $KMnO_4$ solution = 0.1 M

the volume of $KMnO_4$ consumed = V ml

Therefore,

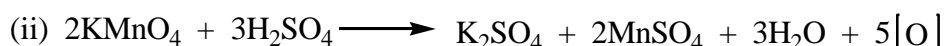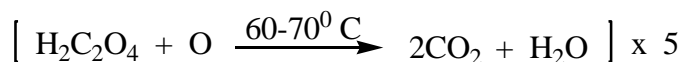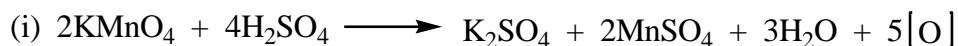$$M_{Fe(II)} = \frac{0.1 \times V}{20} \times \frac{10}{2} \text{ M}$$

So, the amount of Fe(II) in the sample solution = $M_{Fe(II)}$ x 55.85 g

c.Experiment: Estimation of oxalic acid and sodium oxalate in a given mixture.
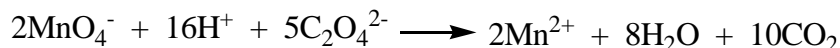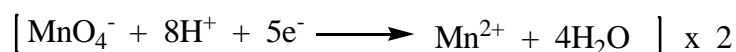
Theory: The mixture solution containing oxalic acid and sodium oxalate is first titrated with 0.05N NaOH solution when only oxalic acid reacts with NaOH.

$$(COOH)_2 + 2NaOH \longrightarrow (COONa)_2 + 2H_2O$$
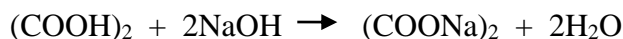
The mixture solution is then again titrated with 0.1N KMnO$_4$ solution when both oxalic acid and sodium oxalate undergo reaction with KMnO$_4$. Thus, the normality of the sodium oxalate can be evaluated by substracting the normality of oxalic acid of the mixture.

(i) $2KMnO_4 + 4H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$\left[H_2C_2O_4 + O \xrightarrow{60\text{-}70^0\,C} 2CO_2 + H_2O \right]$ x 5

$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

(ii) $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$\left[Na_2C_2O_4 + O + H_2SO_4 \longrightarrow Na_2SO_4 + 2CO_2 + H_2O \right]$ x 5

$2KMnO_4 + H_2SO_4 + 5Na_2C_2O_4 \longrightarrow K_2SO_4 + 5Na_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Both reactions (i) and (ii) can be represented in ionic form as follows by the same equation.

$\left[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \right]$ x 2

$\left[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \right]$ x 5

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

Procedure: It involves the following steps:

(i)Titration with NaOH with the mixture: 20 ml of the mixture solution is pipetted out in a conical flask and 2-3 drops of phenolphthalein indicator is added to it. Then this solution is titrated with standardized NaOH solution till the solution turns pink. The titration is repeated to get a set of concordant readings.

(ii)Titration with KMnO₄ with the mixture: 20 ml of the mixture solution is taken in a conical flask. To this one test tube of dilute sulphuric acid is added and the solution is heated to 60-70^0 C and titrated against standardized KMnO$_4$ solution. At the end point, a permanent pink colour appears. The process is repeated to obtain concordant readings.

Calculations:

From titration (i),

Let 20 ml of mixture = V$_1$ ml of 0.05N NaOH

So,

$$N_{oxalic\ acid} = \frac{V_1\ x\ 0.05}{20}\ N$$

$$= \frac{V_1}{400}\ N$$

Therefore, the amount of oxalic acid in the mixture $= \frac{V_1}{400}\ x\ 63\ g$

From titration (ii),

Let 20 ml of mixture $= V_2$ ml of 0.1N $KMnO_4$

So,

$$N_{mixture} = \frac{V_2\ x\ 0.1}{20}\ N$$

$$= \frac{V_2}{200}\ N$$

But,

$$N_{oxalic\ acid} = \frac{V_1}{400}\ N$$

So,

$$N_{sodium\ oxalate} = \frac{V_2}{200}\ N\ -\ \frac{V_1}{400}\ N$$

Therefore, amount of sodium oxalate in the mixture $= \left[\frac{V_2}{200}\ N\ -\ \frac{V_1}{400}\ N \right] x\ 67\ g$

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2. *Advanced Practical Inorganic Chemistry*, Gurdeep Raj; 4th Edition, Goel Publishing House, 2000.
3. *A Textbook of Inorganic Chemistry-I,* B. R. Puri, L. R. Sharma, K. C. Kalia, G. Kaushal; Vishal Publishing Co., Delhi, 2018.

1. Surface tension measurements.

a. Experiment: Determine the surface tension by (i) drop number (ii) drop weight method.

i) Drop number method

Principle: In drop number method, the number of drops formed from the same volume of each liquid is counted. Let the liquid of surface tension γ_1 and density ρ_1 produces n_1 drops whereas the other liquid of surface tension γ_2 and density ρ_2 produces n_2 drops, then:

$$\gamma_1/\gamma_2 = n_2\,\rho_1/n_1\rho_2$$

Requirements: Stalagmometer, weighing bottle, distilled water and pure liquid

Procedure: The Stalagmometer and the beaker are cleaned with warm chromic acid and then with distilled water. It is then rinsed with acetone and dried by current of air. The upper end of the Stalagmometer is mounted at the rubber tube and is fitted in the clamp stand. The lower end is dipped in water and is sucked till it reaches the upper mark and the screw pinch is tightened. Thereafter, the screw is carefully loosened so that liquid drop starts falling at an interval of 2-3 seconds. The number of drops is then counted between two marks. The process is then repeated 3 times and the mean value is taken.

The above procedure is repeated by taking the given liquid in it and the mean value of the number of drops in it is calculated.

Observation:

1)   Density of water at $t^0C = \rho_2$ g/cm^3

        Surface tension of water $= \gamma_2$ dynes /cm

2)   Weight of empty specific bottle $= w_1$ g

        Weight of specific bottle + water $= w_2$ g

        Weight of specific bottle + liquid $= w_3$ g

        Weight of water $= w_2 - w_1$ g

Weight of unknown liquid = $w_3 - w_1$ g

<u>Counting of drops between two marks</u>

Liquid	Number of drops	Average
Water	1. 2. 3.	Mean value (n_2) =
Unknown liquid	1. 2. 3.	Mean value (n_1)=

Calculations:

Determination of density of unknown liquid:

Density of liquid ρ_1/ density of water ρ_2 = (weight of liquid/weight of water)

Density of liquid (ρ_1) = $(w_3 - w_1 / w_2 - w_1)$ x ρ_2 g/cm^3

Surface tension of liquid is given by

$$\gamma_1 = n_2 \, \rho_1 / \, n_1 \rho_2 \, \gamma_2$$

$$= n_2 / n_1 \text{ x } (w_3 - w_1 / w_2 - w_1) \text{ x } \gamma_2 \text{ dynes/cm}$$

Result: The surface tension of the given liquid at t^{0}C = …….. Dynes/cm

ii) Drop weight method

Principle: In this method the weight of 10-20 drops of each liquid is found accurately by the same Stalagmometer. Let m_1 and m_2 be the masses of the drops for the two liquids whose surface tensions are γ_1 and γ_2 respectively then :

$$\gamma_1/\gamma_2 = m_1/m_2$$

Requirements: Stalagmometer, weighing bottle, distilled water, pure liquid, rubber tube,clamp.

Procedure: The Stalagmometer and the beaker are cleaned with warm chromic acid and then with distilled water. It is then rinsed with acetone and dried by current of air. A weighing bottle is placed on the tip of Stalagmometer and a fix number of drops are allowed to fall in it. The rate at which drop falls is adjusted so that each drop falls after 3 seconds. The weight of the weighing bottle and water is determined and from this mass of the drop of water is calculated.

Now the Stalagmometer is cleaned and dried and is filled with given liquid whose surface tension is to be determined and the same process is repeated as above. Knowing the surface tension of water the surface tension of the given liquid can be determined by using the above relation.

Observation and calculations:

Weight of empty weighing bottle = w_1 g

Weight of weighing bottle + 15 drops of water = w_2 g

Weight of weighing bottle + 15 drops of liquid = w_3 g

Weight of   15 drops of water = $w_2 - w_1$ g

Weight of 15 drops of   unknown liquid = $w_3 - w_1$ g

Surface tension of water = γ_2 dynes /cm

Surface tension of liquid = $\gamma_1 \gamma_2$

$$\gamma_1/\gamma_2 = (w_3 - w_1/ w_2 - w_1)$$

$$\gamma_1 = \gamma_2 (w_3 - w_1/ w_2 - w_1) \text{ dynes /cm}$$

Result: The surface tension of the given liquid at t^0C = …….. Dynes /cm

b. Experiment: Study the variation of surface tension of detergent solutions with concentration.

Principle: The surface tension of two liquid constituting mixtures do not differ greatly, the surface tension of the mixture varies directly with the composition. Thus when the surface tension of the mixture is plotted against composition a linear curve is obtained. The concentration of the unknown mixture can be determined by using the Stalagmometer by drop weight method using the relation.

$$\gamma_1/\gamma_2 = m_1/m_2$$

Requirements: Stalagmometer, detergent, weighing bottle, distilled water

Procedure: Detergent solution of different composition say 10%, 20%, 30%, 40% etc. by volume are prepared. The Stalagmometer is dried and cleaned and is filled with distilled water. The weighing bottle is placed below the tip of the Stalagmometer and a fixed number of drops are allowed to fall in it. The weight of the weighing bottle and water is determined. From this mass of the drop of water is found. Now the Stalagmometer is cleaned, dried and filled with detergent solution of known concentration (10%) and the process is repeated as above. Knowing the surface tension of the water at room temperature (γ_1), the surface tension of the 10% solution can be calculated by:

$$\gamma_1 = \gamma_2\, m_1/m_2$$

Surface tension of the detergent solution of different known concentration is found out in similar fashion. A plot is drawn with concentration along x-axis and surface tension along y-axis to get the curve.

Result: From the curve obtained, concentration of known solution can be determined.

2. Viscosity measurement using Ostwald's viscometer.

a. Experiment: Determination of viscosity of aqueous solutions of (i) polymer (ii) ethanol and (iii) sugar at room temperature.

Theory: The co-efficient of viscosity (η_2) of given aqueous solution is determined by making use of the following formula:

$$\eta_1/\eta_2 = \rho_1 t_1/\rho_2 t_2$$

Where ρ_1 = density of water at room temperature

ρ_2 = density of given aqueous solution at room temperature

η_1 = viscosity of water at room temperature

Also t_1 and t_2 are the times of flow of water and the given aqueous solution for the same volume of the two liquids through the fine capillary.

Requirements: Viscometer, stopwatch, beaker, clamp, pipette, a long rubber tubing, distilled water, specific gravity bottle and thermometer.

Procedure: Clean the Ostwald viscometer thoroughly first with chromic acid and then with running tap water and finally with distilled water. Rinse it with acetone or ether and dry it with hot air from hot-air blower. It is then mounted vertically and a definite volume of water is introduced into bulb B and is sucked into A, above the mark P. The water then flows down the capillary and the time t_2, required to fall from mark P to Q is noted accurately using a stopwatch. A mean of three observations is recorded. The experiment is repeated with given liquid and the corresponding time t_1 is also noted.
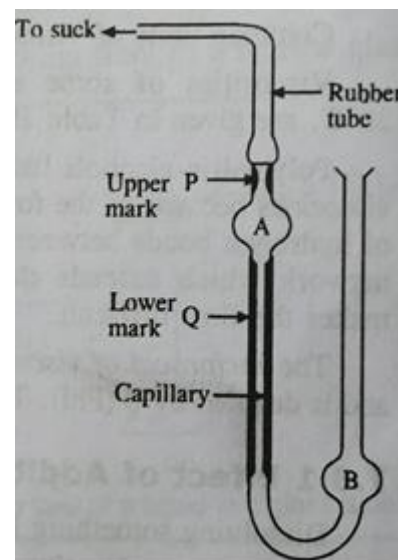

Fig. Ostwald's viscometer

Observation:

Room temperature = t^0C

Density of water at t^0C, $\rho_{1\ =\ ....}$

Viscosity of water at t^0C, $\eta_{1\ =\ ....}$ Poise

	Water		Unknown liquid	
Sl. No.	Time of flow in seconds	Mean value	Time of flow in seconds	Mean value
1.			1.	
2.		t_2=	2.	t_1=
3.			3.	
4.			4.	

Observation and calculations:

Weight of empty weighing bottle = w_1 g

Weight of weighing bottle + water = w_2 g

Weight of weighing bottle + liquid = w_3 g

Weight of   water = $w_2 - w_1$ g

Weight unknown liquid = $w_3 - w_1$ g

Surface tension of water = γ_2 dynes /cm

Surface tension of liquid = $\gamma_1 \, \gamma_2$

$$\rho_1 / \rho_2 = (w_3 - w_1 / w_2 - w_1)$$

The Co-efficient of viscosity of the liquid is given by

$$\eta_1 = \rho_1 t_1 / \rho_2 t_2 \times \eta_2$$

The relative viscosity of the liquid is given by

$$\eta_1 / \eta_2 = \rho_1 t_1 / \rho_2 t_2$$

By putting the respective values, the relative viscosity of liquid is calculated

$$\eta_1 = (w_3 - w_1) \, t_1 / (w_2 - w_1) \, t_2 \times \eta_2$$

Thus η_1 can be calculated

Result: The Co-efficient of viscosity of the liquid is ……… poise

b. Experiment: Study the variation of viscosity of sucrose solution with the concentration of solute.

Requirements: Sucrose, viscometer, stopwatch, beaker, clamp, pipette, a long rubber tubing, distilled water, specific gravity bottle and thermometer.

Theory: The co-efficient of viscosity(η_2) of given aqueous solution is determined by making use of the following formula:

$$\eta_1 / \eta_2 = \rho_1 t_1 / \rho_2 t_2$$

Where ρ_1 = density of water at room temperature

ρ_2 = density of given aqueous solution at room temperature

η_1 = viscosity of water at room temperature

Also t_1 and t_2 are the times of flow of water and the given aqueous solution for the same volume of the two liquids through the fine capillary.

Procedure: A rubber tube is attached to a cleaned and dried viscometer and it is clamped to a stand. 15 ml of water is introduced into the larger bulb B of the viscometer. It is then sucked into the bulb till it rises to the mark P. The time of flow of water, t_1, from mark P to Q is noted by using a stopwatch.
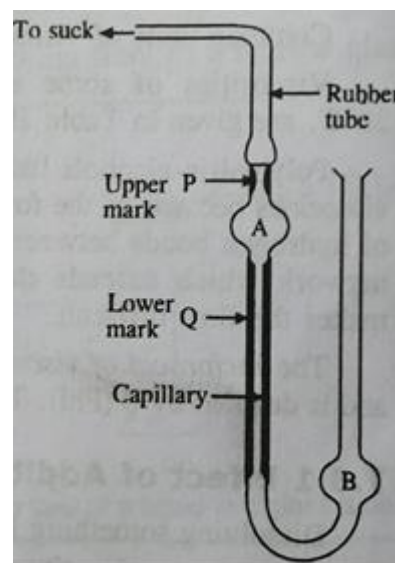

Fig. Ostwald's viscometer

The viscometer is then dried. A series of aqueous solution of sucrose of different compositions i.e. viscosity of each sucrose solution is determined and a graph plotted between viscosity and composition. From the graph, the composition corresponding to the viscosity of sucrose solution with unknown composition can be determined.

Observation and calculations:

Room temperature = t^0C

Time of flow of the solvent = ………., Mean = t_2

Density of pure solvent = ρ_2

**For solutions:**

Concentrations	Flow time				Density (ρ)	η
	(i)	(ii)	(iii)	Mean (t sec)		
2%						
4%						
6%						
8%						
10%						

A graph is plotted between concentration of sucrose along x axis and corresponding viscosity along y axis. From the shape of curve obtained, the variation with concentration can be studied. From the plot the composition corresponding to the viscosity/ time of flow of unknown liquid can be determined.

3. pH metry

a. Experiment: Study the effect on pH of addition of HCl/NaOH to solutions of acetic acid, sodium acetate and their mixtures.

Theory: Acetic acid is a weak acid, it dissociates to a very small extent.
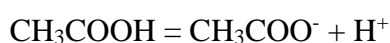
$$CH_3COOH = CH_3COO^- + H^+$$

When a few drops of HCl solution is added to acetic acid solution, there will be increase in H^+ ion concentration, thus the above equilibrium shift towards left. There is suppression in the degree of ionization of acetic acid. Further addition of HCl to acetic acid solution will continuously increase H^+ concentration and pH of the solution will decrease continuously.

When a few drops of strong base i.e. NaOH are added, the OH^- ions added are neutralized by the acetic acid. There will be very little change in the pH. Also some CH_3COOH-CH_3COONa buffer formed, which resist some change in pH to a certain level .But further addition of NaOH solution will continuously increase the pH of the solution.

Requirements: 1.0 M HCl, 1.0 M NaOH, 1.0 M CH_3COOH, 1.0 M CH_3COONa, pH meter, buffer

Solutions (pH = 4 and 9), distilled water, thermometer, beakers, pipette, burette.

Procedure: The pH electrode is rinsed with distilled water and it is calibrated against a buffer known pH. A 0.10M acetic acid solution is prepared by measuring out 10.0 ml of the 1.0 M acetic acid in a 100ml graduated cylinder and then distilled water is added to get a final volume of 100ml.

The 0.10 M acetic acid solution is divided into two 50ml portion. To the first portion 1 ml of HCl solution is mixed and the pH is recorded. To the second portion 1 ml of NaOH solution is mixed and the pH is recorded.

Same procedure is repeated with sodium acetate and mixture of acetic acid and sodium acetate.

Observation and calculations:

Room temperature = t^0C

Solution	Initial pH	pH after addition of 1.0 ml of 1.0 M HCl	pH after addition of 1.0 ml of 1.0 M NaOH
1. 0.10 M CH$_3$COOH 2. 0.10 M CH$_3$COONa 3. 0.10 M CH$_3$COOH + 0.10 M CH$_3$COONa			

b. Experiment: Preparation of buffer solutions of different pH

i. Sodium acetate-acetic acid

Theory: Acetic acid is a weak acid, it dissociates to a very small extent.
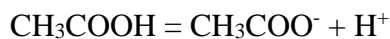
$$CH_3COOH = CH_3COO^- + H^+$$

When a few drops of HCl solution is added to acetic acid solution, there will be increase in H$^+$ ion concentration, thus the above equilibrium shift towards left. There is suppression in the degree of ionization of acetic acid. Further addition of HCl to acetic acid solution will continuously increase H$^+$ concentration and pH of the solution will decrease continuously.

When a few drops of strong base i.e. NaOH is added, the OH$^-$ ions added are neutralized by the acetic acid. There will be very little change in the pH. Also some CH$_3$COOH-CH$_3$COONa buffer formed, which resist some change in pH to a certain level. But further addition of NaOH solution will continuously increase the pH of the solution.

Requirements: CH$_3$COOH, 1.0 M CH$_3$COONa, pH meter, buffer solutions (pH = 4 and 9), distilled water, thermometer, beakers, pipette, burette.

Procedure: 0.2 M CH$_3$COONa and 0.2 M CH$_3$COOH is prepared. With this stock solution, buffers of different pH values ranging from 3.42 to 5.49 can be prepared. Different volume of

0.2 M CH$_3$COONa and 0.2 M CH$_3$COOH are mixed and pH values are recorded. It is observed that by decreasing the volume of acetic acid and increasing the volume of sodium acetate slightly, the buffer with higher and higher pH values is obtained.

| 0.2 M CH$_3$COOH	0.2 M CH$_3$COONa	pH
9.5	0.5	3.42
9.0	1.0	3.72
8.0	2.0	4.05
7.0	3.0	4.27
6.0	4.0	4.45
5.0	5.0	4.63
4.0	6.0	4.80
3.0	7.0	4.88
2.0	8.0	5.23
1.0	9.0	5.57
0.5	9.5	5.89

ii. Ammonium chloride-ammonium hydroxide

Theory: An alkaline buffer solution has a pH greater than 7. They are commonly prepared from a weak base and one of its salts. A frequent used example is a mixture of ammonia solution and ammonium chloride solution. If these were mixed in equal molar proportions, the solution would have a pH of 9.25. Thus, a mixture containing equimolar ammonium hydroxide and ammonium chloride is a good alkaline buffer. The mixture contains undissociated NH$_4$OH as well as NH$_4^+$ and Cl$^-$ ions. The buffer action of this mixture may now be considered.

If a strong acid is added, the H$^+$ ions added are neutralized by the base NH$_4$OH:

$$H^+ + NH_4OH \quad \text{----------> } H2O \ + \ NH_4^+$$
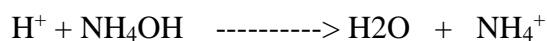
If a strong base is added, the OH⁻ ions added are neutralized by NH_4^+ ions forming very slightly dissociated NH_4OH.

$$OH^- + NH_4^+ \quad \text{----------> } NH_4OH$$
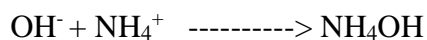
In this case the reversible acidity is due to the presence of NH_4^+ ions and reserve alkalinity is due to the presence of NH_4OH.

The pH of a buffer solutions consisting of a weak base and its salt can be calculated by using Henderson equation.

$$pOH = pK_b + \log [salt] / [base]$$

Further, $\qquad pOH + pH = 14$

Requirements: Standard HCl solution, NH_4Cl, NH_4OH, methyl orange indicator, pH meter, burette, pipette, thermometer, buffer solutions, beakers.

Procedure: 100 ml of 0.4 M NH_4OH is prepared and then it is standardized with 0.4 M HCl solution using methyl orange as indicator. From this NH_4OH, 100 ml of 0.2 M is prepared by taking required amount from standardized 0.4 M NH_4OH and diluting it to 100 ml with addition of distilled water. 100 ml of 0.2 M NH_4Cl is prepared. A series of different buffer solution is prepared by mixing 0.2 M NH_4Cl and 0.2 M NH_4OH and then pH value of each solution is calculated using pH meter. The theoretical pH value is also calculated using Henderson equation.

Observation:

pK_b of NH_4OH = 4.74

Sl. No.	Volume of 0.2 M NH₄OH (ml)	Volume of 0.2 M NH₄Cl (ml)	pOH = pK_b + log [salt] / [base]	pH =14 - pOH	pH
1	9	1			
2	8	2			
3	7	3			

4	6	4			
5	5	5			
6	4	6			
7	3	7			
8	2	8			
9	1	9			

Calculations:

 For buffer 1,

$$pOH = pK_b + \log [salt] / [base]$$

$$pOH = 4.74 + \log 1 / 9 = 4.74 + (- 0.95) = 3.78$$

$$pH = 14 – 3.78 = 10.22$$

For buffer 2,

$$pOH = 4.74 + \log 2 / 8 = 9.86$$

And so on.

c. Experiment: pH metric titration of strong acid vs. strong base

Theory: On addition of small amount of base to an acid solution, the concentration of H^+ will decrease and pH will increase. In the beginning pH will increase slowly but at equivalence point, it increases rapidly owing to rapid increase in the fraction of H^+ ions removed by the addition of constant volume of alkali. At the equivalence point, pH decreases slowly. Thus a plot of pH vs. volume of alkali can be drawn.

Requirements: 0.1 N HCl solution, 0.1 N NaOH solution, pH meter, burette, pipette, thermometer, buffer solutions of known pH , distilled water.

Procedure: HCl and NaOH solutions are standardized and pH METER is calibrated with buffer solutions of known pH. 20 ml of 0.1 N HCl solution is taken in a beaker and the pH is

measured. 0.5 ml lots of 0.1 N NaOH solution is added in to the HCl solution and pH is measured after each addition. The pH is measured till 25 to 30 ml of NaOH solution is added.

Observation:

Room temperature = t°C

Volume of HCl solution taken for titration = 20 ml

Sl. No.	Volume of 0.1 N NaOH solution	pH
1	0	…
2	0.5	…
3	1.0	
4	1.5	…
5	2.0	…
…	…	…
…	…	…
…	…	…
…	…	…
…	…	…
…	30.0	…

Calculations: A graph is plotted taking pH values on y- axis and the volume of NaOH added (in mL) on the x-axis. From the curve obtained the volume of titrant used for the neutralization of 20 ml of 0.1 N HCl i.e. equivalence point.

Calculation of normality of HCl solution

Volume of 0.1 N NaOH used for the neutralization of 20 ml of 0.1 N HCl = V_2 mL

Here, Normality of HCl solution = N_1

Volume of HCl solution = V_1

Normality of NaOH solution = N_2

Applying normality equation

$$N_1V_1 = N_2V_2$$

$$N_1 \text{ x } 20 = 0.1 \text{ x } V_2$$

$$N_1 = 1/20 \text{ x } 0.1 \text{ x } V_2$$

$$N_1 = V_2/200 \text{ N}$$

Calculation of strength of HCl solution

$$\text{Strength} = \text{Normality x Equivalent mass}$$

$$= V_2/200 \text{ x } 36.5 \text{ g/ litre}$$

Result: Strength of given HCl solution = ……… g/ litre

d. Experiment: Determination of dissociation constant of a weak acid (CH_3COOH) pH metrically

Requirements: 0.1 N CH_3COOH solution, 0.1 N NaOH solution, pH meter, burette, pipette, thermometer, buffer solutions of known pH , distilled water.

Theory: According Bronsted-Lowry acid base theory, the strength of an acid is related to its ability to donate protons. Acetic acid is a weak acid and dissociates partially in aqueous solution. The general equation for the ionization of a weak acid may be represented as

$$HA \quad + \quad H_2O \quad <====> H_3O^+ \quad + \quad A^-$$
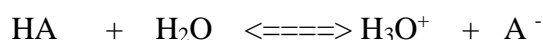
The dissociation constant, K_a for the dilute solutions of the weak acids

$$K_a = [H_3O^+] [A^-] / [HA]$$

where $[H_3O^+]$ is the concentration of H^+ ions , $[A^-]$ is the concentration of anions ,[HA] is the concentration of unionized acid.

$$\text{Or} \quad [H_3O^+] = K_a [HA] / [A^-]$$

We know $\qquad\qquad\qquad$ $pH = \log [H_3O^+]$

$$\text{Or} \quad -\log[H_3O^+] = -\log K_a - \log[HA]/[A^-]$$

$$\text{Or} \quad pH = pK_a - \log[HA]/[A^-]$$

If we titrate weak acid HA with base there will be a point, where one half the base needed to neutralize the weak acid has been added, the molar concentration of weak acid [HA] and conjugate base [A⁻] are equal. The hydronium ion concentration measured at 50 % neutralization is equal to the dissociation constant of the weak acid i.e.

$$\text{i.e.} \quad [HA] = [A^-], \text{ ratio } [HA]/[A^-] = 1$$

$$\log[HA]/[A^-] = 0$$

$$\text{Therefore,} \quad pH = pK_a$$

Procedure: CH_3COOH and NaOH solutions are standardized and pH meter is calibrated with buffer solutions of known pH. 20 ml of 0.1 N HCl solution is taken in a beaker and the pH is measured. 0.5 ml lots of 0.1 N NaOH solution is added in to the HCl solution and pH is measured after each addition. The pH is measured till 25 to 30 ml of NaOH solution is added.

Observation:

Sl. No.	Volume of NaOH solution	pH	$\Delta pH/\Delta V$
1	0	…	
2	0.5	…	
3	1.0	…	
4	1.5	…	
5	2.0	…	
…	…	…	
…	…	…	
…	…	…	
…	…	…	
…	…	…	
…	30.0	…	

Calculations:

To determine dissociation constant of acetic acid

At neutralization, volume of NaOH used = Z mL

At half neutralization = Z/2 mL

pH = …..   (At half neutralization)

At half neutralization,   [Acid] = [Salt]

i.e. $pH = pK_a$

$pH = - \log K_a$

Hence, dissociation constant K_a of acetic acid can be determined.

Result: Dissociation constant K_a of acetic acid = ………….

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