Determination of the rate constant for the hydrolysis of ester

Short Procedure

1. Prepare 500 ml of approximately 0.1 (N) NaOH solution.

2. Standardize the alkali solution by taking 2 ml of supplied oxalic acid solution, using phenolphthalein indicator. [The candidate must use the same 2 ml pipette, as needed, throughout this kinetic experiment.]

3. Take 50 ml of the supplied catalyst solution in a 100ml dry conical flask, add 5 ml of ester using a pipette and note the time of half discharge.

4. At 2 – 3 minutes regular interval (for first four readings) and then 5 minutes intervals for next readings) take 2 ml aliquot and 50 ml distilled water (*ice/ice-cold water not to be used*) taken in a 250 ml conical flask. Titrate rapidly against the prepared 0.1 (N) NaOH solution taken in a burette, using phenolphthalein as indicator. Take at least 6 readings.

5. V-infinity reading: Calculate the V_α from the following expression:

   V_α (**in ml**) = 4.56/y where y = strength of the NaOH in **normality**, used in the experiment.

6. Plot the graph using the experimental data and determine "k" from the graph.

Decomposition of Hydrogen Peroxide

Short Procedure

1. Prepare 250 ml of approximately 0.1 (N) sodium thiosulphate solution in a glass bottle. Fill the burette with sodium thiosulphate solution.

2. Take (using a measuring cylinder) 10 ml of supplied H_2SO_4 in a 500 ml conical flask. Add 10 ml (using the 10ml pipette) of the supplied H_2O_2 solution and then approximately 2 gm solid KI. Add about 50 ml of water. Add 2 ml of supplied 1& ammonium molybdate solution. Cover the conical flask with a watch glass and keep it for approximately 1 minute. Add about 50 ml of water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator. Record the titre value (V_o).

3. Take 250 ml (use a volumetric flask) of supplied KI solution and transfer it to a 500 ml conical flask. Add 15 ml of supplied sulphuric acid and 5 ml of freshly prepared starch solution. Add 10 ml of supplied H_2O_2 solution (using a 10ml pipette) and note the half-discharge time. Run immediately sodium thiosulphate solution from the burette into the mixture in excess to discharge the blue colour. Wait for the reappearance of the blue colour and record the time of appearance of the colour. Volume of the thiosulphate added gives V_i.

4. Again run thiosulphate solution into the mixture in excess to discharge the blue colour completely and then wait for the reappearance of colour. Record the time of appearance of the colour and total volume of the thiosulphate solution used.

5. Take at least 6 consistent readings. Plot $\log \dfrac{V_o}{V_o - V_t}$ vs t. Calculate "k" value from the graph.

Kinetic Study of the Iodination of Acetone

Theory

If a solution of iodine is added to dilute solution of acetone then iodination of acetone takes place. But the reaction is fairly slow in dilute acid solution. If we add an excess of iodine and then titrate the iodine left in the solution by sodium thiosulphate solution at different times then the continuous diminution in the titre value will indicate the amount of iodine consumed by acetone.

With respect to iodine this is a zero order reaction na d may be represented by the equation

$$\frac{dx}{dt} = k \qquad \text{or} \qquad x = kt + c$$

When $t = 0$, $x = 0$; hence $c = 0$.   So $k = x/t$

Therefore, $k = x_1/t_1 = x_2/t_2 = $ etc.

Hence $x_2 - x_1 = k(t_2 - t_1)$ or $\Delta x = k\Delta t$ or $k = \Delta x/\Delta t$

Now, $(a - x_1) = (V_1 \text{ x } S_{thio})/V_{aliquot}$ and $(a - x_2) = (V_2 \text{ x } S_{thio})/V_{aliquot}$

or, $\Delta x = x_2 - x_1 = \{(V_1 - V_2) \text{ x } S_{thio}\}/V_{aliquot} = (\Delta V \text{ x } S_{thio})/V_{aliquot}$

So, $k = \Delta x/\Delta t = \dfrac{\Delta V}{\Delta t} \dfrac{S_{thio}}{V_{aliquot}}$

Slope of the plot of ΔV against Δt gives $\Delta V/\Delta t$

So if x (i.e. $V_i - V_t$ where V_i and V_t are the volume of thiosulphate required at time "zero" and time "t" respectively) is plotted against time, the slope of the curve will give the value of "k", the specific reaction rate. Alternatively, V_t may be plotted against "t" or ΔV may be plotted against Δt.

Short Procedure

1. Into a mixture of 150 ml water, 20 ml acetone and 10ml 1(N) H_2SO_4, 25 ml 0.1(N) iodine solution was added. The time of half-discharge was noted and it was mixed well. 25 ml of reaction mixture was taken out and it was transferred to 20 ml $NaHCO_3$ solution taken in a conical flask. The time of half-discharge was noted and the solution was titrated with (N/50) $Na_2S_2O_3$. This procedure was repeated for several times at an interval of ~3 minutes.

2. The experiment was performed with a 2nd set of different composition.

   Set I: 150ml H_2O + 20 ml Acetone + 10 ml 1(N) H_2SO_4 + 25 ml 0.1(N) I_2

   Set II: 150ml H_2O + 20 ml Acetone + 10 ml 0.5(N) H_2SO_4 + 25 ml 0.1(N) I_2

3. $(V_i - V_t)$ against time (or ΔV against Δt or V_t against t) was plotted in each case and the values of k were determined from each plot.

4. The $Na_2S_2O_3$ solution was standardized with a standard $K_2Cr_2O_7$ solution to get the absolute values of k.

5. From the ratios of different values of k it was shown that the reaction is independent of the concentration of iodine but dependent on the concentration of acetone and acid.

Study of kinetics of $K_2S_2O_8$ + KI reaction, spectrophotometrically

Short Procedure

1. Standardize the supplied ~ N/10 sodium thiosulphate solution iodometrically using starch solution as indicator. [Take 10 mL of **_supplied_**, standard N/10 $K_2Cr_2O_7$ solution in a 500 mL conical flask. Add about 15 mL (approximately one test tube) of ~ 10% KI solution and ~ 20 mL of ~ 4(N) HCl solution. Cover the conical flask with watch glass and keep in dark for about 5 minutes. Add ~ 150 mL of distilled water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator].

2. Standardize the supplied $K_2S_2O_8$ solution (of strength greater than N/10) using the following procedure. [Take 10 mL of the supplied $K_2S_2O_8$ solution in a 250 mL conical flask; add 20 mL of ~ 10% KI solution and 2 mL of glacial acetic acid. **_Prepare two sets at the same time_**. Cover the conical flask with watch glass and keep the mixture in the dark for 45 minutes. Add 50 mL of water and titrate the liberated iodine against the standard thiosulphate solution using starch solution as indicator].

3. Prepare 50 mL of an exact N/10 $K_2S_2O_8$ solution from the standardized $K_2S_2O_8$ solution by quantitative dilution.

4. Prepare 50 mL of an exact N/10 KI solution by exact weighing. [Alternatively, prepare 100 mL solution of KI solution of strength greater than N/10; then prepare 100 mL of exact N/10 KI solution by quantitative dilution of this solution].

5. Set up the colorimeter and adjust properly the **SET – 0** and **SET – 100** controls, using the filter at **525 nm** (peak wavelength).

6. Pipette out 10 mL of the exact N/10 $K_2S_2O_8$ solution in a clean, dry 100 mL beaker. Add 10 mL of the exact N/10 KI solution to this solution by the same pipette and note the half – discharge time as t = 0.

7. Note the absorbance (A) of the reaction mixture at **525 nm** (peak) wavelength at an interval of 1 minute for 15 readings.

8. Plot **1/A** versus **1/t** for the reaction mixture and calculate the rate constant from the graph.

Determination of Molecular Weight of Polyvinyl alcohol (PVA) by Viscometric Measurement

Theory

Viscometric method is a simple and widely used method for molecular weight determination of polymer. The viscosity of polymer solution can be accurately measured and it is different from that of the solvent.

Let the viscosity of pure solvent $= \eta_o$
Let the viscosity of pure polymer solution $= \eta$
Then, the *relative viscosity* of pure polymer solution, $\eta_{rel} = \eta / \eta_o$
Remember that, $\eta / \eta_{o} = \rho(t/t_o)$
(*where, ρ is the specific gravity of the polymer solution; t and t_o are the time of flow of the polymer solution and water, respectively, through the same viscometer*).

The *specific viscosity* of polymer solution, η_{sp} $= \dfrac{(\eta - \eta_o)}{\eta_o}$

The *reduced viscosity* of polymer solution, η_{red} $= \eta_{sp} / C$
The *intrinsic viscosity* of polymer solution, $[\eta]$ $= (\eta_{red})_{C \to 0}$
$$= \left[\frac{(\eta - \eta_o)}{\eta_o C} \right]_{C \to 0}$$

The intrinsic viscosity of polymer solution is related to molecular weight of polymer according to the following relation,

$$[\eta] = KM^{\alpha}$$

(*where K and α are constants and M is the molecular weight*)

[The constants K and α can be determined by taking polymer of known molecular weight].
If a graph of η_{red} vs. concentration of polymer solution (C) is plotted, a straight line is obtained. From the intercept we can determine the molecular weight of polymer.

Short Procedure

1. Prepare 100 mL 1% solution of PVA by dissolving 1 g of the polymer in hot water.
2. From this 1% solution of PVA prepare 50 mL each of 0.75%, 0.50%, 0.25% and 0.125% PVA solution by exact dilution.
3. Rinse the viscometer thoroughly with distilled water and the take 10 mL (or 15 mL) water (using pipette) in the viscometer and measure the time of flow between the two marks. Repeat the process, note the time of flow and evaluate the average time of flow. Also take the weight of empty specific gravity bottle and weight of the specific gravity bottle filled with water.
4. Repeat step – 3 for all the five polymer solution (i.e. 1%, 0.75%, 0.5%, 0.5% and 0.125% PVA solution) using the same viscometer and measure the time of flow between the two marks for each solution. Also, take the weight of specific gravity bottle filled with polymer solution of different strength. Determine the specific gravity of each solution.
5. Calculate η_{sp} / C and plot η_{sp} / C vs. C (C = concentration of polymer solution) for each solution. Calculate η_{red} at $C \to 0$ (i.e. calculate the intercept of η_{sp} / C vs. C plot).
6. Knowing the value of $[\eta]$, determine the molecular weight of the polymer using the relation $[\eta] = KM^{\alpha}$. [Given: **K = 45..3 x 10^{-3}** and **α = 0.64** at 29°C]

Using a conductometer, verify Ostwald's dilution law of a weak acid and determine the ionization constant (K_a) and the equivalent conductance at infinite dilution (λ_0) of that weak acid

A. Write down the theory of the experiment highlighting the following points:

(i) Conductance, cell constant, specific conductance, equivalent conductance – definition and interrelation.

(ii) Principle of determination of cell constant.

(iii) Variation of equivalent conductance of the solution of a weak acid with dilution, and its explanation.

(iv) Derivation of Ostwald's dilution law and the working formula for this experiment.

(v) Determination of K_a and λ_0 from the plot of $1/\lambda$ versus λc (where, c is the concentration of the weak acid, using proper temperature correction).

B. Short Procedure:

(i) Prepare exactly 100 mL oxalic acid solution {of the order of (N/10)} by exact dilution of supplied 1(N) oxalic acid solution.

(ii) Prepare approximately 200 mL of ~(N/10) NaOH solution by dilution of supplied ~1(N) NaOH solution and standardize the NaOH solution against the prepared standard oxalic acid solution (using phenolphthalein indicator).

(iii) Standardize the supplied ~(N/10) weak acid solution against the standard NaOH solution solution (using phenolphthalein indicator)..

(iv) Prepare 100 mL of an exact 0.01(N) KCl from supplied exact 0.1(N) KCl. Determine the cell constant of the conductivity cell using the supplied exact 0.1(N) KCl and the prepared exact 0.01(N) KCl. 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.

(v) Prepare 250 mL of exact (N/50) weak acid solution from the standardized solution using the supplied conductivity water. With the help of a 25 mL pipette, take 50 ml of this solution in the clean and dry conductivity cell and measure its conductance.

(vi) Use the same 25 mL pipette to take out 25 mL of the (N/50) weak acid solution from the conductivity cell (without lifting the conductivity cell). Pipette out 25 mL 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.

(vii) Follow the procedure of step – vi to prepare in situ exact (N/200), (N/400), (N/800) and (N/1600) weak acid solutions in steps and note their conductances.

(viii) 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.

(ix) From the plot of $1/\lambda$ versus λc calculate the λ_0 form 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.*

pH of Buffer by Colour Matching Method

Short Procedure

1. Prepare 250 ml of an exactly 0.4(N) acetic acid solution using the supplied exactly 5(N) acetic acid (use a pipette to transfer the acid).

2. Prepare 250 ml of approximately 0.5(N) NaOH solution in a 250 ml glass bottle.

3. Standardize the prepared NaOH solution against the 0.4(N) acetic acid solution taking 10ml of the acid as aliquot and using phenolphthalein as indicator.

4. Determine the strength of the alkali. Prepare 100ml of exact 0.4 (N) NaOH solution by quantitative dilution.

5. Take 10 dry, test tubes of approximately equal diameter. Label them from 1 to 9 and prepare the following buffer solutions by proper mixing of exact 0.4(N) NaOH and 0.4(N) acetic acid.

Test tube number	Volume of 0.4(N) acetic acid (ml)	Volume of 0.4(N) NaOH (ml)	Volume of water (ml)	Total volume (ml)	pH
1	5.0	0.5	4.5	10.0	3.72
2	5.0	1.0	4.0	10.0	4.05
3	5.0	1.5	3.5	10.0	4.27
4	5.0	2.0	3.0	10.0	4.45
5	5.0	2.5	2.5	10.0	4.63
6	5.0	3.0	2.0	10.0	4.80
7	5.0	3.5	1.5	10.0	4.99
8	5.0	4.0	1.0	10.0	5.23
9	5.0	4.5	0.5	10.0	5.57

6. In the remaining test tube, pipette out exactly 10 ml of the buffer solution supplied to you, marked "BF". To each of these test tubes add 3 drops of the indicator provided. Mix thoroughly to develop uniform colour in each test tube. Identify the pH of the supplied buffer solution (BF) by colour matching.

Determination of pH of unknown buffer using an indicator and determination of pK$_{In}$ (indicator constant), spectrophotometrically

Short Procedure

1. Prepare approximately 200 mL of ~ N/2 NaOH solution by dilution of supplied ~1(N) NaOH solution.
2. Prepare approximately 150 mL N/2 acetic acid solution by dilution from supplied ~ 1(N) acetic acid solution.
3. Standardize the NaOH solution by supplied exactly 1 (N) oxalic acid solution as follows. *Pipette out 10 mL of exactly 1(N) oxalic acid solution in a 100 mL conical flask. Titrate this solution against ~ N/2 NaOH solution (taken in a burette) using phenolphthalein indicator (2 – 3 drops).*
4. Standardize the ~ N/2 acetic solution, with 10 mL aliquot, against the standardized NaOH solution (taken in a burette) using phenolphthalein indicator (2 – 3 drops).
5. Prepare 100 mL exactly 0.4(N) acetic acid solution and 100 mL exactly 0.4(N) NaOH solution by quantitative dilution.
6. Take 12 glass tubes of uniform diameter and label then 1 to 12. Prepare the following series of buffer solutions (of acetic acid and sodium acetate) in these test tubes by proper mixing.

Test tube number	Volume of exactly 0.4(N) acetic acid solution	Volume of exactly 0.4(N) NaOH solution	Volume of H$_2$O	pH of the buffer solution
1	5 mL	0.5 mL	4.5 mL	3.72
2	5 mL	1.0 mL	4.0 mL	4.05
3	5 mL	1.5 mL	3.5 mL	4.27
4	5 mL	2.0 mL	3.0 mL	4.45
5	5 mL	2.5 mL	2.5 mL	4.63
6	5 mL	3.0 mL	2.0 mL	4.80
7	5 mL	3.5 mL	1.5 mL	4.99
8	5 mL	4.0 mL	1.0 mL	5.23
9	5 mL	4.5 mL	0.5 mL	5.57
For test tube labelled 10, 11 and 12, take 2.5 mL of exactly 0.4(N) NaOH solution and 7.5 mL of water.				

7. Set up the colorimeter and adjust properly the **SET – 0** and **SET – 100** controls, using the filter at *570 nm* (peak wavelength). Add a measured number of drops of the supplied indicator solution to the test tube labelled "10". Mix thoroughly. Set the colorimeter at *570 nm* (peak). Measure the **% T** of the solution taken in test tube 10. Adjust the number of drops of indicator to get the **% T** within 15% to 25%, using the solution in test tube 11 and 12. Note the number of drops of indicator added (**n**) to get the value of %T within 15 to 25. Also, note the %T of this solution. Calculate the Absorbance of this solution. It is denoted as **A$_{Alk}$**.
8. Add the same number of drops (**n**) as adjusted, in the test tube 1 to 9. Mix thoroughly.
9. Measure the absorbance (**A**) of the buffer solutions (containing the indicator) in test tube 1 to 9.
10. Pipette out 10 mL of supplied buffer solution (of unknown strength) in a clean and dry test tube. Add same drops of indicator as has been added to test tube labeled 1 to 9 and measure its absorbance (**A$_{unknown}$**) also.
11. Plot **pH** versus **log [A/(A$_{alk}$ – A)]**. Using the curve, determine the pH of the supplied buffer solution and from the slope and intercept of the curve, calculate the **pK$_{In}$** of the indicator at room temperature.

Using a Conductometer to determine the rate constant of saponification reaction of methyl acetate at room temperature

A. **Write down the theory of the experiment highlighting the following points:**

(i) The chemical reaction, order of the reaction; integrated rate equation for rate equation for reactions of that order, with explanation of all the terms appearing; unit of k.

(ii) Deduction of the working formula from the integrated equation.

(iii) Variation of conductance of reaction mixture with time and its explanation.

(iv) Determination of the rate constant for the reaction from the working formula graphically.

B. **Short Procedure:**

(i) Prepare 100 mL oxalic acid solution {of the order of (N/10)} by exact dilution of supplied 1(N) oxalic acid solution.

(ii) Prepare approximately 250 mL of ~(N/10) NaOH solution by dilution of supplied ~1(N) NaOH solution and standardize the NaOH solution against the prepared standard oxalic acid solution (using 10 mL standard oxalic acid and phenolphthalein indicator).

(iii) Dilute the standardized NaOH solution to prepare 100 mL exact (M/60) NaOH solution (using distilled water).

(iv) Prepare 100 mL of a ~ (N/10) acetic acid solution from the supplied ~ 1(N) acetic acid solution. Standardize 10 mL of it against the standardized ~ (N/10) NaOH solution (using phenolphthalein). From the standardized solution, prepare 100 mL exact (M/60) acetic acid solution by proper dilution.

(v) Take a 100 mL volumetric flask with about 50 mL of distilled water. Transfer into this exactly 1.0 mL of the supplied pure methyl acetate, using a 1 mL graduated pipette and make up the volume with distilled 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^o C)
$$= [0.932 - \{(t - 20) \times 1.25 \times 10^{-4}\}] \text{ g/mL}$$
Prepare an exact (M/60) methyl acetate solution from this standard methyl acetate solution by proper dilution with distilled water.

(vi) Prepare 50 mL exact (M/120) NaOH solution from exact (M/60) NaOH solution by proper dilution with distilled water and note its conductance as C_o.

(vii) Mix 25 mL each of (M/60) NaOH and (M/60) acetic acid solutions and note its conductance as C_∞.

(viii) Take 25 mL (M/60) methyl acetate and add 25 mL (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 1 minute. Take at least 15 readings.

(ix) Plot (C_o – C_t) / (C_t - C_∞) versus time to obtain the rate constant of the reaction at room temperature.