
UNIT 15 INTEGRATED RATE EQUATION METHOD

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15.1 INTRODUCTION

In Unit 14 we determined some simple kinetic parameters like order, rate constant, etc. of two reactions by the initial rate method. Although the initial rate method is easy to carry out, this method may not reveal the full rate law in a complex reaction. Sometimes the products themselves may get involved in intermediate steps. For example, in the synthesis of HBr, the true rate law involves the concentration of HBr. But HBr being a product is not present initially. A study of this reaction by the initial rate method will give the rate only in terms of amount of hydrogen and bromine, thus not giving the correct rate equation. To avoid this, the rate law should be fitted to the data throughout the course of the reaction. In order to do so, we can use the integrated rate equations and, try to fit the data collected during the entire reaction or a good part of the reaction. In this unit, we will study the procedures for the following five experiments for obtaining the order and/or rate constant of different reactions using the integrated rate equation method.

- (i) Two experiments on the kinetics of iodination of acetone, one by titrimetry and another by colorimetry
- (ii) One experiment on the kinetics of acid catalysed hydrolysis of ester by titrimetry
- (iii) Two experiments on the kinetics of saponification of ester, one by titrimetry and another by conductometry.

Finally the preparation of solutions used in Experiments 17–21 is discussed in the appendix.

Objectives

After performing the experiments mentioned in this unit, you should be able to:

- study experimentally the kinetics of simple reactions using titrimetry, colorimetry and conductometry,
- explain Ostwald's isolation method,
- describe the use of graphical method in determining the order of reaction, and
- fit the experiment data into an integrated rate equation to obtain the rate constant of a reaction.

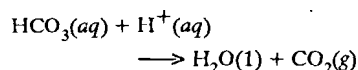
15.2 EXPERIMENT 17 : KINETICS OF IODINATION OF ACETONE — TITRIMETRY

15.2.1 Principle

In aqueous solution, acetone and iodine react according to the equation:



Quenching : Quenching is the process of stopping or slowing down a chemical reaction suddenly by lowering temperature or by adding a reagent which consumes one of the reactants or the catalyst. In the iodination of acetone, the addition of reaction mixture to NaHCO_3 solution more or less stops the reaction due to consumption of H^+ ions and the liberation of carbon dioxide gas.



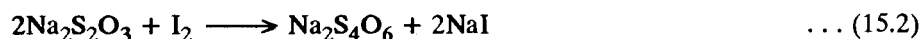
Both acids and bases catalyse this reaction. The iodination of acetone occurs rapidly at both high pH and low pH but occurs only slowly around pH 7. The kinetics of this reaction in acid solution can be conveniently studied by measuring the concentration of iodine as a function of time during the reaction. The reaction mixture is prepared by adding iodine into a mixture of acetone and hydrochloric acid starting the stop watch simultaneously. Then samples of the reaction mixture are withdrawn at known times, discharged into sodium hydrogen carbonate solution for **quenching** the reaction. The iodine remaining is titrated with sodium thiosulphate solution. From the titre values, the concentration of iodine remaining is calculated. Using graphical method, the order of reaction with respect to iodine, acetone and the mineral acid is found out. The rate constant is also finally calculated.

We shall first discuss the calculation of concentration of iodine using the titrimetric method.

Integrated Rate Equation Method

Calculation of concentration of iodine in the reaction mixture.

The unreacted iodine in the reaction mixture is estimated by titrating it with standardised sodium thiosulphate solution as per the reaction:



To determine the end point in the titration, starch solution is added, when the titrated mixture is pale yellow in colour. That is, the starch is added towards the end point. If starch solution is added much earlier to the end point, then the starch gets coagulated and, the end point cannot be determined accurately. The end point is the disappearance of violet colour formed by the interaction between starch and iodine.

Let us represent the molarity and volume of sodium thiosulphate by M_1 and V_1 , and, those of iodine (in the reaction mixture) by M_2 and V_2 , respectively.

Using Eq. 1.13 of Unit 1 of this course, we can write

$$\frac{M_1 V_1}{M_2 V_2} = \frac{2}{1} \quad \dots (15.3)$$

since the stoichiometric coefficients of $\text{Na}_2\text{S}_2\text{O}_3$ and I_2 are 2 and 1, respectively as per Eq. 15.2.

Hence, molarity of iodine in the reaction mixture,

$$M_2 = \frac{M_1 V_1}{2V_2} \quad \dots (15.4)$$

Eq. 15.4 is used for calculating the concentration of iodine $[\text{I}_2]$ in the reaction mixture at various time intervals. From $[\text{I}_2]$ values, those of $\log [\text{I}_2]$ and $1/[\text{I}_2]$ can also be calculated at various time intervals using logarithmic tables. Next, let us discuss the generalised form of rate equation for the iodination of acetone.

Rate Equation

The generalised form of rate equation for the iodination of acetone is given below:

$$\frac{-d[\text{I}_2]}{dt} = k[\text{I}_2]^x [\text{CH}_3\text{COCH}_3]^y [\text{H}^+]^z \quad \dots (15.5)$$

where x , y and z are orders of reaction in iodine, acetone and H^+ ions, respectively and, k is the rate constant of iodination of acetone.

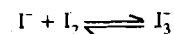
Note that we are measuring the amount of iodine remaining as a function of time; the rate hence determined is $-d[\text{I}_2]/dt$. As we are interested in getting the orders x , y and z individually, we are going to use the Ostwald's isolation method.

Ostwald's isolation method : This is a convenient method for the determination of order of reaction when more than one reactant is present. To determine the order of reaction in one reactant, all the other reactants are taken in excess and the kinetics is studied. The experiment is repeated to find the order of reaction with respect to each reactant. If you want to know more about isolation method, go through Sec. 18.7 of Unit 18 of CHE-04 course.

We will next study the principles behind the determination of order of reaction with respect to each species.

Sodium hydrogen carbonate should be pure and, should not contain sodium carbonate, since aqueous sodium carbonate solution could also react with iodine. Instead of sodium hydrogen carbonate solution, sodium acetate solution can also be used.

Iodine is dissolved in excess of potassium iodide which yields potassium triiodide.



Both I_2 and I_3^- are effective iodinating agents for acetone. The treatment of results is unaffected when I_2 is substituted for I_3^- .

Order of reaction in iodine (x)

In keeping with isolation method, we will take acetone in excess concentration, that is, choose the condition such that $[\text{acetone}] \gg [\text{I}_2]$. Under these conditions, the change in the concentration of acetone during the reaction will be negligible; that is, $[\text{acetone}]$ remains almost constant during the course of the reaction. The rate equation (Eq. 15.5) gets modified to:

$$\frac{-d[\text{I}_2]}{dt} = k_a [\text{I}_2]^x \text{ where } k_a = k [\text{CH}_3\text{COCH}_3]_a^y [\text{H}^+]_a^z \quad \dots (15.6)$$

We have included $[\text{H}^+]$ along with the constants because H^+ being a catalyst remains unconsumed. Also, $[\text{CH}_3\text{COCH}_3]_a$ and $[\text{H}^+]_a$ stand for the respective concentrations in Experiment 17(a).

We shall perform the kinetic run as per the details given in the procedure under Experiment 17(a) to determine the order in iodine (x). We shall calculate the concentration of iodine ($[\text{I}_2]_t$) in the reaction mixture at various time intervals, t . We shall enter the values in the observation table I under Sec. 15.2.4

We shall use graphical method for the determination of order in iodine. In Subsec. 13.3.2 of Unit 13, the graphical method of arriving at the order of reaction has been discussed. Accordingly, the types of plots expected for zeroth order, first order and second order kinetics with respect to iodine are given below:

- Graph (i) : $[\text{I}_2]_t$ against t for zeroth order
 Graph (ii) : $\log [\text{I}_2]_t$ against t for first order
 Graph (iii) : $1/[\text{I}_2]_t$ against t for second order

We have to try all these three plots. The order of reaction in iodine corresponds to that plot which gives a straight line. Note that all the above plots are made using the data in observation Table I under Sec. 15.2.4.

You shall see that the zeroth order plot (i.e., $[\text{I}_2]_t$ against t plot), gives a straight line. That is, the reaction is zeroth order in iodine or $x = 0$. Hence, Eq. 15.6 can be written as,

$$\frac{-d[\text{I}_2]}{dt} = k_a \text{ where } k_a = k [\text{CH}_3\text{COCH}_3]_a^y [\text{H}^+]_a^z \quad \dots (15.7)$$

$$\text{since } [\text{I}_2]^x = [\text{I}_2]^0 = 1$$

For determining y and z (orders of reaction in acetone and H^+), we shall use modified form of Eq. 15.7.

Further, we can determine k_a from the slope of $[\text{I}_2]_t$ against t plot, (graph (i)), since the reaction is zeroth order with respect to iodine. This can be understood by comparing the integrated equation for a zeroth order reaction with the equation for a straight line.

$$\left. \begin{array}{l} \text{Integrated equation for} \\ \text{zeroth order reaction as per Eq. 15.7} \\ \text{(and Table 13.1 of Unit 13)} \end{array} \right\} : [\text{I}_2]_t = [\text{I}_2]_0 - k_a t \quad \dots (15.8)$$

$[\text{I}_2]_0$ and $[\text{I}_2]_t$ stand for the concentration of iodine in the reaction mixture at the start and, after a time interval, t .

$$\text{Equation for a straight line : } (y = c + mx) \quad \dots (15.9)$$

Hence from Eqs. 15.8 and 15.9,

$$\text{slope} = m = -k_a$$

$$\text{or } k_a = -\text{slope of graph (i)} \quad \dots (15.10)$$

Hence the slope of graph (i) of Experiment 17(a) gives k_a as per Eq. 15.10. Hence from Experiment 17(a), we shall find

(i) that the order of the reaction in iodine is zero,

$$\text{i.e. } x = 0$$

(ii) the value of k_a from Eq. 15.10 as, $k_a = -\text{slope of graph(i)}$. Next let us determine the order of reaction in acetone.

Determination of Order of Reaction in Acetone (y)

Experiment 17(b) is performed to determine the order of reaction in acetone. The concentrations of iodine and H^+ in Experiment 17(b) are maintained same as in Experiment 17(a). But the concentration of acetone is reduced to half the concentration of acetone taken in Experiment 17(a).

$$\left. \begin{array}{l} [H^+]_b = [H^+]_a \\ [I_2]_b = [I_2]_a \end{array} \right\} \dots (15.11)$$

and $[CH_3COCH_3]_b = \frac{1}{2} [CH_3COCH_3]_a$

Similar to Eq. 15.7, we can write

$$\frac{-d[I_2]}{dt} = k_b \text{ where } k_b = k [CH_3COCH_3]_b^y [H^+]_b^z \dots (15.12)$$

where k_b is the constant to be obtained from Experiment 17(b).

In Experiment 17(b), the concentrations of iodine in the reaction mixture are determined at various time intervals and the values are entered in observation table II under Sec. 15.2.7. Using $[I_2]_t$ and t values at various time intervals, graph (iv) is plotted ($[I_2]_t$ against t plot). The slope of graph (iv) gives k_b as per Eq. 15.13.

$$k_b = -\text{slope of graph (iv)} \dots (15.13)$$

From k_a and k_b , we can obtain y as follows. Using Eq. 15.11 in Eq. 15.12, we can write,

$$k_b = k ([CH_3COCH_3]_a/2)^y [H^+]_a^z$$

i.e. $k_b = (1/2)^y k [CH_3COCH_3]_a^y [H^+]_a^z$

using Eq. 15.7, $k_b = k_a (1/2)^y \dots (15.14)$

Taking logarithms, $\log k_b = \log k_a + y \log 1/2$

or $\log k_b - \log k_a = -y (0.3010)$

$$\log k_b/k_a = -0.3010 y$$

i.e., $y = -\frac{\log k_b/k_a}{0.3010}$

$$y = \frac{1}{0.3010} \log \frac{\text{slope of graph (iv)}}{\text{slope of graph (i)}} \dots (15.15)$$

[since $\frac{k_b}{k_a} = \frac{-\text{slope of graph (iv)}}{-\text{slope of graph (i)}}$ as per Eqs. 15.10 and 15.13]

Hence, the order in acetone (y) can be calculated from the slopes of plots in Graphs (i) and (iv).

Integrated Rate Equation Method

In Table 13.1 of Unit 13 of this course, generalised form of integrated rate equation (Eq. 15.8) is given.

For understanding the straight line plots, see Sec. 2.6 of Unit 2 of this course

Order of reaction in H^+ (z)

To determine the order in H^+ , Experiment 17(c) is performed. In Experiment 17(c), $[H^+]$ is reduced to half the value in Experiment 17(a). Otherwise, the concentrations of iodine and acetone in Experiment 17(c) are maintained the same as in Experiment 17(a).

$$\text{i.e., } \left. \begin{aligned} [H^+]_c &= 1/2 [H^+]_a \\ [I_2]_c &= [I_2]_a \\ [CH_3COCH_3]_c &= [CH_3COCH_3]_a \end{aligned} \right\} \dots (15.15)$$

Similar to Eq. 15.12, we can write,

$$\frac{-d[I_2]}{dt} = k_c \text{ where } k_c = k [CH_3COCH_3]_c^y [H^+]_c^z \dots (15.17)$$

In Experiment 17(c), the concentrations of iodine in the reaction mixture are determined at various time intervals and the values are entered in Observation Table III under Sec. 15.2.10. Then $[I_2]_t$ against t plot (Graph (v)) is made. The slope of Graph (v) gives k_c as per Eq. 15.18.

$$k_c = -\text{slope of graph (v)} \dots (15.18)$$

From k_a and k_c , we can obtain z as follows:

Using Eqs. 15.16 and 15.17, we can write

$$k_c = k [CH_3COCH_3]_a^y ([H^+]_a/2)^z \dots (15.19)$$

Using steps similar to those used in obtaining Eq. 15.15 from Eq. 15.14, we can obtain Eq. 15.20 from Eq. 15.19.

$$\begin{aligned} \text{i.e., } z &= \frac{-\log k_c/k_a}{0.3010} \\ &= -\frac{1}{0.3010} \log \frac{\text{slope of graph (v)}}{\text{slope of graph (i)}} \dots (15.20) \end{aligned}$$

Thus we could find out x , y and z . Finally we shall calculate the rate constant k for the iodination of acetone using Eq. 15.6 and the data under Experiment 17(a).

$$k = k_a / [CH_3COCH_3]_a^y [H^+]_a^z \dots (15.21)$$

Hence by substituting for k_a and initial concentrations of acetone and H^+ from Experiment 17(a), we can calculate k .

15.2.2 Requirements

Apparatus	Chemicals
Burettes (50 cm ³) – 3	Acetone
Pipettes graduated (20 cm ³) – 3	Iodine
Conical flasks (250 cm ³) – 2	Potassium iodide
Conical flasks (100 cm ³) – 7	Hydrochloric acid
Boiling tube – 1	Sodium hydrogen carbonate
Test tube – 1	Sodium thiosulphate
Beaker (250 cm ³) – 1	Starch
Beaker (400 cm ³) – 1	Deionised water

- Wash bottle (with deionised water) – 1
- Burette stands (with clamps) – 3
- Thermometer – 1
- Stopwatch – 1
- Water trough/Thermostat – 1

Solutions that are provided for all the three experiments, (17(a), 17(b) and 17(c):

1. 0.05 M I₂ in 0.4 M KI
2. 1.0 M HCl
3. 0.10 M NaHCO₃
4. 0.01 M Na₂S₂O₃
5. Starch solution 1%

Details for the preparation of the solution are given in Appendix.

15.2.3 Procedure for Experiment 17(a)

Determination of the Order of Reaction in Iodine

1. Bring to your work – table all the required apparatus and solutions as given under 15.2.2.
2. Rinse and fill burette 1 with sodium thiosulphate solution.
3. Rinse and fill burette 2 with 1 M HCl.
4. Rinse and fill burette 3 with deionised water.
5. Pipette out 10 cm³ of 0.1 M NaHCO₃ solution into each of five 100 cm³ conical flasks.
6. Withdraw into a 250 cm³ conical flask from the burettes 10 cm³ of 1 M HCl and 70 cm³ of deionised water. Pipette into this, 10 cm³ of acetone and stopper the flask.
7. Pipette 10 cm³ of iodine solution into a boiling tube and stopper it. Keep both the 250 cm³ conical flask and the boiling tube in a water trough (or thermostat). Note the temperature.
8. Pour the iodine solution into the flask containing acetone, HCl and water, starting the stop watch at the same time. Mix well by pouring from one into the other.
9. Withdraw 10 cm³ of the reaction mixture and run this sample into the flask containing 10 cm³ of NaHCO₃ solution, noting the time when the pipette is half empty. Mix well by shaking and then titrate the residual iodine with Na₂S₂O₃ solution till the solution becomes pale yellow in colour. Add 2 cm³ of starch solution. Continue titrating this blue solution with Na₂S₂O₃ till the solution turns colourless (end point). Note the burette reading.
10. Repeat the titration of 10 cm³ samples of the reaction mixture giving an interval of about 2 minutes between sampling.
11. After the titration is over, wash the flasks with large quantities of water because the reaction mixture contains iodoacetone, a powerful lachrymator.
12. Calculate [I₂]_t, log[I₂]_t and 1/[I₂]_t and enter these in Observation Table I.
13. Plot [I₂]_t vs *t*, log[I₂]_t vs *t* and 1/[I₂]_t vs *t* as Graphs (i), (ii) and (iii), respectively.

100 cm³ reaction mixture is made from

- | | | |
|--|-----|-------------------------------|
| (i) 10 cm ³ of 1 M HCl | } | in 250 ml
conical
flask |
| (ii) 70 cm ³ of water (deionised) | | |
| (iii) 10 cm ³ of acetone | | |
| | and | |
| (iv) 10 cm ³ of the solution– | | in a boiling tube. |

If the reaction mixture is at 35°C, then 2–3 minute intervals are suitable. If the students work in pairs, they will be able to manage doing titrations at 2 minutes interval. For performing titrations at 5–7 minutes interval at 35°C, the concentrations of HCl and (or) of acetone may be decreased. This instruction holds good for Experiments 17(a), (b) and (c). On the other hand if the temperature is 25°C, 5–7 minute intervals could be given.

Even with two 100 cm³ flasks, the experiment can be performed.

Lachrymator is a substance that stimulates formation of tears.

15.2.4 Observation for Experiment 17(a)

Molarity of thio (M_1) = M

Volume of the reaction mixture withdrawn at each time t (V_2) = 10 cm^3

As per Eq. 15.4, $[I_2]$ in the reaction mixture = $[I_2]_t$

$$= M_2 = \frac{M_1 V_1}{2V_2} = \frac{M_1 V_1}{20}$$

(since $V_2 = 10 \text{ cm}^3$)

Volume of NaHCO_3 solution taken for quenching the reaction = 10 cm^3

Solution taken in the burette = $0.01 \text{ M Na}_2\text{S}_2\text{O}_3$

Volume of starch solution added just before the end point = 2 cm^3

Temperature of the reaction mixture =°C

Observation Table - I

t/s	Burette reading		(Volume of thio (V_1))/ cm^3	$[I_2]_t/M$ $= \frac{M_1 V_1}{20}$	$\log [I_2]_t/M$	$\frac{M}{[I_2]_t}$
	Initial	Final				

15.2.5 Calculations for Experiment 17(a)

Draw inference from the graphs (i), (ii) and (iii) about the order of the reaction in iodine. Also obtain the slope of Graph (i).

The order of the reaction in iodine is

Using Eq. 15.10, $k_a = -\text{slope of graph (i)}$
 $= \dots\dots M \text{ s}^{-1}$

15.2.6 Procedure for Experiment 17(b)

Determination of the Order of Reaction in Acetone

Repeat instructions 1 to 5 and 7 to 11 as in Experiment 17(a) under Sec. 15.2.3. In the place of instruction (6), do the following: Withdraw into a 250 cm^3 conical flask from the burettes, 10 cm^3 of 1 M HCl and 75 cm^3 of deionised water. Pipette into this, 5 cm^3 of acetone and stopper the flask. That is, we take in this experiment half the concentration of acetone taken in Experiment 17(a). You can withdraw reaction mixture at 7–10 minutes interval and do the titration against standardised thio.

Calculate $[I_2]_t$ at various intervals and enter the data in observation table II. Also plot $[I_2]_t$ against t (Graph iv).

100 cm^3 reaction mixture contains

- (i) 10 cm^3 of 1 M HCl
 - (ii) 70 cm^3 of water (deionised)
 - (iii) 5 cm^3 of acetone
 - and
 - (iv) 10 cm^3 of iodine solution – in a boiling tube.
- } in 250 ml conical flask

15.2.7 Observation for Experiment 17(b)

Observation Table – II

t/s	Burette reading		(Volume of thio (V_1))/cm ³	$[I_2]_t/M^*$	$= \frac{M_1 V_1}{20}$
	Initial	Final			

* Use M_1 value from Experiment 17(a).

15.2.8 Calculation for Experiment 17(b)

From Graph (iv), find out the slope of the line.

From Eq. 15.13, $k_b = -\text{slope of Graph (iv)}$

$$= \dots M s^{-1}$$

Order of the reaction in acetone = y

$$\text{(using Eq. 15.15)} = -\frac{1}{0.3010} \log \frac{\text{slope of graph (iv)}}{\text{slope of graph (i)}}$$

100 cm³ reaction mixture contains

- | | |
|---|---------------------------|
| (i) 5 cm ³ of 1 M HCl | } in 250 ml conical flask |
| (ii) 75 cm ³ of water (deionised) | |
| (iii) 10 cm ³ of acetone | |
| and | |
| (iv) 10 cm ³ of iodine solution - in a boiling tube. | |

15.2.9 Procedure for Experiment 17(c)

Determination of the Order of Reaction in H⁺ ions

Repeat instructions 1 to 5 and 7 to 11 as in Sec. 15.2.3 under Experiment 17(a). In place of instruction 6 do as follows:

Withdraw into a 250 cm³ conical flask from the burettes, 5 cm³ of 1 M HCl and 75 cm³ of deionised water. Pipette into this, 10 cm³ of acetone and stopper the flask. That is, we take half the concentration of hydrochloric acid taken in Experiment 17(a). You can withdraw reaction mixture at 7–10 minutes interval and do titration against standardised thiosulphate solution.

Calculate $[I_2]_t$ at various intervals and enter the data in observation Table III. Also plot $[I_2]_t$ against t (graph v).

15.2.10 Observation for Experiment 17(c)

Observation Table – III

t/s	Burette reading		(Volume of thio (V_1))/cm ³	$[I_2]_t/M^*$	$= \frac{M_1 V_1}{20}$
	Initial	Final			

* Use M_1 value from Experiment 17(a).

Chemical Kinetics

$[H^+]$ is 0.1 M since in Experiment 17(a), 10 cm³ of 1 M HCl is made up to 100 cm³ (as reaction mixture)

$[CH_3COCH_3]_a$ is equal to 1.36 M as per the calculation indicated below:

The reaction mixture contains 10 cm³ of acetone in a total volume of 100 cm³ in Experiment 17(a).

$[CH_3COCH_3]_a$

$$= \frac{\left\{ \begin{array}{l} \text{Molarity of} \\ \text{acetone in} \\ \text{Experiment 17(a)} \end{array} \right\}}{\text{Mass of acetone}} \\ = \frac{\text{(molar mass} \times \text{(volume of solution of acetone) in dm}^3\text{)}}{\dots (16.22)}$$

$$\begin{aligned} \text{Mass of acetone} &= (\text{Volume of acetone} \\ &\quad \times \text{density of acetone}) \\ &= 10 \text{ cm}^3 \times 0.79 \text{ g cm}^{-3} \\ &= 7.9 \text{ g} \end{aligned}$$

$$\text{Volume of solution} = 100 \text{ cm}^3 = 0.1 \text{ dm}^3 \\ \text{(reaction mixture)}$$

$$\text{Molar mass of acetone} = 58.08 \text{ g mol}^{-1}$$

Substituting these in Eq. 15.22,

$$\begin{aligned} [CH_3COCH_3]_a &= \frac{7.9 \text{ g}}{58.08 \text{ g mol}^{-1} \times 0.1 \text{ dm}^{-3}} \\ &= 1.36 \text{ mol cm}^{-3} \\ &= 1.36 \text{ M} \end{aligned}$$

15.2.11 Calculation for Experiment 17(c)

From graph (v), find out the slope of the line.

From Eq. 15.18, $k_c = -\text{slope of graph (v)} = \dots M s^{-1}$

From Eq. 15.20, the order of the reaction in H^+

$$= z = -\frac{1}{0.3010} \log \frac{\text{slope of graph (v)}}{\text{slope of graph (i)}}$$

We can also calculate the rate constant of iodination of acetone, k .

$$\text{From Eq. 15.21, } k = \frac{k_a}{[CH_3COCH_3]_a [H^+]_a}$$

But $k_a = -\text{slope of graph (i)}$ (using Eq. 15.10)

Also, $[CH_3COCH_3]_a = 1.36 \text{ M}$ and $[H^+]_a = 0.1 \text{ M}$

Hence

$$\begin{aligned} k &= \frac{k_a}{(1.36)^y (0.1)^z} \\ &= \dots M^{1-(y+z)} \\ & \quad [M \text{ stands for molarity unit}]. \end{aligned}$$

15.2.12 Result

Order of the reaction in iodine = x =
Order of the reaction in acetone = y =
Order of the reaction in H^+ ions = z =
Rate constant for the iodination of acetone = k =

15.2.13 Precautions

1. Laboratory samples of acetone often contain peroxides which liberate iodine from acidified KI. This produces a small amount of iodine in the reaction mixture. But the liberated iodine is getting used up in the main reaction. The peroxides thus get destroyed and the data obtained after the first 1–2 minutes give a linear graph (Inclusion of data obtained in the first 1–2 minutes gives a curvature to the line).
2. Iodoacetone, a product of the reaction is a very powerful lachrymator. All solutions containing this should be disposed of immediately after the experiment, and the apparatus washed with plenty of water.
3. Iodine solution and acetone should be kept in well stoppered bottles.
4. Sodium thiosulphate solution and starch solution should be prepared on the same day the experiment is to be done.

15.3 EXPERIMENT 18 : THE ORDER OF IODINATION OF ACETONE IN IODINE – COLORIMETRY

15.3.1 Principle

The kinetics of acid catalysed iodination of acetone (Eq. 15.1) is to be followed colorimetrically in this experiment. We shall confine ourselves to the determination of order of reaction in iodine only. It is our aim to familiarise you with the colorimetric method of following the kinetics of iodination reaction.

You will be using low-cost colorimeter for performing the experiment. Although, iodine forms triiodide ion (I_3^-) in presence of iodide, both I_2 and I_3^- have same absorption pattern. Both of them iodinate acetone. Hence what we are going to measure is the total concentration of I_2 and I_3^- . Again, the total concentration of I_2 and I_3^- is proportional to absorbance as per Beer-Lambert law. When you use a low-cost colorimeter, you measure meter reading (R) values which are proportional to absorbance as well as to concentration of iodine.

Since we are interested in finding only the order of the reaction in iodine but not the actual rate constant, it is not necessary to examine the reaction in terms of $[I_2]_t$. It is enough to study the reaction in terms of meter reading values. Hence, instead of using $[I_2]_t$, $\log [I_2]_t$ and $1/[I_2]_t$, we will be using the corresponding meter reading values, viz., R_t , $\log R_t$ and $1/R_t$.

To find the order of the reaction in iodine, we will try zeroth order, first order and second order plots as shown below:

R_t against t plot : for zeroth order reaction
 $\log R_t$ against t plot : for first order reaction
 $1/R_t$ against t plot : for second order reaction.

You will see that R_t against t plot gives a much better straight line, which brings out the zero order dependence in I_2 concentration.

15.3.2 Requirements

Apparatus	Chemicals
Burettes (50 cm^3) - 4	Acetone
Beakers (250 cm^3) - 1	Iodine
Test tubes (20 cm^3) - 10	Potassium iodide
Colorimeter - 1	Hydrochloric acid
Stopwatch - 1	Deionised water
Thermometer - 1	
Wash bottle (with deionised water) - 1	
Burette stands with clamps - 4	
Water trough/Thermostat - 1	

Solutions that are needed for this experiment:

1. $0.05 \text{ M } I_2$ in 0.4 M KI
2. 1.0 M HCl
3. 4 M Acetone

Details for the preparation of the solution are given in Appendix.

15.3.3 Procedure

1. Plug the colorimeter into the mains and switch it on.
2. Keep the colour selector knob at green. (If it is a commercial colorimeter, use the green filter. If it is a spectrophotometer, adjust the wavelength knob to read 565 nm .)
3. Take a clean cuvette, make a mark at the top on one plain side, if it is already not marked. Rinse and fill it with deionised water. Wipe the outside dry with tissue paper.
4. Insert the cuvette into the cuvette holder with the marked side facing the LEDs. (In a commercial instrument, the mark on the cuvette should be made to coincide with the mark outside on the holder). Everytime you insert the cuvette into the holder, maintain this position.
5. Adjust the set zero knob till the meter reads zero.
6. Then mix 3 cm^3 of iodine solution and 7 cm^3 of deionised water in a boiling tube. After mixing the solution thoroughly, rinse and fill the same cuvette

with this iodine solution. Wipe the outside dry with tissue paper. Insert into the holder.

7. Adjust the sensitivity knob till the meter reads somewhere near the end of the scale, say 8. After this adjustment, **do not disturb the sensitivity knob** for the rest of the entire experiment. You do steps 8 and 9 only if you are working with a low cost colorimeter.
8. Rinse and fill the same cuvette with deionised water. Wipe the outside dry and insert into the holder. If the meter does not read zero, then adjust the set zero knob till it reads zero. After this adjustment, **do not disturb the set zero knob** for the rest of the entire experiment.
9. Withdraw from the burettes, 4 cm³ deionised water, 2 cm³ of hydrochloric acid and 2 cm³ of acetone solution into a 250 cm³ beaker.
10. Withdraw 2 cm³ of iodine solution from the burette into a test tube. **Keep the beaker and the test tube in a water trough (or a thermostat) and note the temperature.**
11. Pour the iodine solution into the solution in the beaker, starting the stop-watch at the same time. Mix well by pouring one to the other.
12. Rinse the cuvette with the reaction mixture, fill with the same, wipe the outside, insert into the holder noting the mark on the cuvette.
13. Hold the stopwatch close to the meter and read the stop-watch as the needle passes by marked divisions on the meter-scale. (Avoid taking reading when the needle is in between divisions). Note 8- 10 such meter readings and the corresponding time readings. Enter these in the observation Table IV.
14. Remember that iodoacetone is a powerful lachrymator. Hence discard all solutions containing this and, wash your glass apparatus with plenty of water.
15. Calculate $\log R_t$ and $1/R_t$ and enter these in the same Table.

10 cm³ reaction mixture is made as follows:

- | | | |
|--|---|---------------------------------------|
| (i) 4 cm ³ of deionised water | } | in a
250 cm ³
beaker |
| (ii) 2 cm ³ of 1 M HCl | | |
| (iii) 2 cm ³ of 4 M acetone | | |
| (iv) 2 cm ³ of 0.05 M iodine - in a
test tube solution | | |

15.3.4 Observation

Temperature of the reaction mixture =..... °C

Observation Table - IV

t/s	R_t	$\log R_t$	$1/R_t$

15.3.5 Calculation

Plot three graphs: 1) graph (vi): R_t vs t ; 2) graph (vii): $\log R_t$ vs t ; and 3) graph (viii): $1/R_t$ vs t . Infer the order of the reaction in I₂ from the graphs.

The order of the reaction in iodine =

15.3.6 Result

The order of the reaction in iodine =

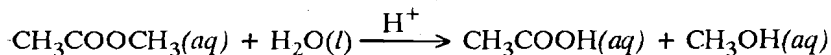
15.3.7 Precautions

The first three precautions given in the previous experiment also apply here. Further, the adjusted knobs should not be disturbed during the experiment.

15.4 EXPERIMENT 19 : KINETICS OF ACID CATALYSED HYDROLYSIS OF ESTER – TITRIMETRY

15.4.1 Principle

The hydrolysis of an ester is quite slow and reversible. But this reaction is catalysed by acids and alkalies. In this experiment, we shall study the hydrolysis of methyl acetate in presence of hydrochloric acid.



This reaction is an example of pseudo first order reaction. The concentration of water is high and, it almost remains constant throughout the reaction. The concentration of mineral acid which catalyses the reaction also remains constant. Thus the reaction rate depends only on the concentration of ester.

$$\text{i.e., Rate} = k [\text{CH}_3\text{COOCH}_3] \quad \dots (15.23)$$

Using the integrated rate equation for a first order reaction as given in Table 14.1 of Unit 14, we can write,

$$k = \frac{2.303}{t} \log \frac{c_0}{(c_0 - x)} \quad \dots (15.24)$$

where c_0 is the initial concentration of the ester and $(c_0 - x)$ is the concentration of the ester at a time, t . Let us next discuss the outline of this experiment.

We mix known amounts of the ester and the mineral acid and withdraw equal volumes of the reaction mixture at definite intervals into vessels containing ice-cold water. The ice-cold water is added to decrease the rate of the reaction. The reaction mixture so withdrawn is titrated against standardised alkali using phenolphthalein as the indicator. The end point is the appearance of pink colour which does not disappear within ten seconds. From the titre values at various time intervals, the rate constant is calculated using the procedure indicated below:

The reaction mixture withdrawn each time contains a definite amount of hydrochloric acid and also acetic acid formed due to hydrolysis. Each titre value represents by the volume of sodium hydroxide solution required to neutralise both these acids.

Suppose that V_0 , V_t and V_∞ are the titre values initially, at a time t and at the end of the reaction (infinite reading). V_0 is proportional to the amount of hydrochloric acid present in a definite volume of reaction mixture, when no acetic acid is formed.

V_∞ is proportional to the amount of hydrochloric acid, and acetic acid present in a definite volume of reaction mixture after the completion of the reaction.

V_t is proportional to the amount of hydrochloric acid and acetic acid present in a definite volume of reaction mixture after a time, t .

$(V_\infty - V_0)$ is proportional to the amount of acetic acid formed when hydrolysis is complete or it is proportional to the initial concentration of ester (c_0)

$$\text{i.e., } (V_\infty - V_0) \text{ is proportional to } c_0 \quad \dots (15.25)$$

Similarly, $(V_t - V_0)$ is proportional to the acetic acid formed at a time t or is proportional to the concentration of ester hydrolysed (x) at a time, t .

Hence the concentration of ester remaining unhydrolysed at a time t (i.e., $(c_0 - x)$) is proportional to

$$[(V_\infty - V_0) - (V_t - V_0)]$$

i.e., $(c_0 - x)$ is proportional to $(V_\infty - V_t)$... (15.26)

Using Eqs. 15.24 to 15.26,

$$k = \frac{2.303}{t} \log_{10} \frac{(V_\infty - V_0)}{V_\infty - V_t} \quad \dots (15.27)$$

or $\log_{10} (V_\infty - V_t) = \log (V_\infty - V_0) - \frac{k_t}{2.303}$... (15.28)

k can be calculated either by substituting V_0 , V_t and V_∞ into Eq. 15.27 or by graphical method. For calculation by graphical method, $\log_{10} (V_\infty - V_t)$ is plotted against t . As per Eq. 15.28, this should give a straight line plot, the slope being equal to $-k/2.303$.

In other words, $k = -2.303 \times \text{slope}$... (15.29)

15.4.2 Requirements

Apparatus

50 cm ³ Burettes	- 2
100 cm ³ conical flasks	- 4
250 cm ³ conical flask	- 1
5 cm ³ pipettes	- 2
Stopwatch	- 1

Copper water bath	- 1
Thermometer	- 1
Water trough/Thermostat	- 1

Solutions that are needed for this experiment:

0.5 M hydrochloric acid
0.125 M sodium hydroxide
Phenolphthalein indicator solution

Chemicals

Methyl acetate
Hydrochloric acid
Phenolphthalein
Sodium hydroxide
ice water (prepared from carbon dioxide free water)

Details for the preparation of the solution are given in Appendix.

15.4.3 Procedure

- Using a 50 cm³ burette, take 50 cm³ of 0.5 M hydrochloric acid in a 250 ml conical flask.
- Pipette out 5 cm³ of methyl acetate in a test tube and keep both the conical flask and the test tube in a water trough (or a thermostat) for about five minutes.
- Transfer the ester to the conical flask containing hydrochloric acid. Start the stop-watch when nearly half the volume of ester has been added.
- After complete transfer, shake the mixture in the conical flask.
- Immediately pipette out 5 cm³ of the mixture into a 100 cm³ conical flask containing 25 cm³ of ice-cold water. Add a drop of phenolphthalein and titrate the resultant solution against 0.125 M sodium hydroxide solution. The end point is the appearance of light pink colour.
- The first titre value represents V_0 and enter this in observation Table V. At intervals of 10 minutes upto 1 hour, repeat the process of pipetting 5 cm³ of reaction mixture into a conical flask containing 1 drop of phenolphthalein and 25 cm³ of ice-cold water and, titrating against 0.125 M sodium hydroxide solution. Enter the titre values in observation table V. Each of the titre values from second onwards constitute V_t .

55 cm³ of the reaction mixture is prepared from

- 50 cm³ of 0.5 M hydrochloric acid - taken in a 250 cm³ conical flask
- 5 cm³ of methyl acetate - taken in a test tube

- 7) After taking six readings, pipette out 10 cm³ of a mixture into a 100 cm³ conical flask and close it with a loose cork. Heat the conical flask on a copper water bath at 50°C for about 30 minutes. Then cool the conical flask to room temperature and titrate 5 cm³ of this mixture against 0.125 M sodium hydroxide solution using phenolphthalein as indicator. The last titre value represents the infinite reading (V_{∞}).

15.4.4 Observation

Room temperature = °C

Observation Table - IV

t/s	Burette reading		Titre value	$\log (V_{\infty} - V_t)/\text{cm}^3$
	Initial	Final		

15.4.5 Calculation

Using Eq. 15.27, $k = \frac{2.303}{t} \log \frac{(V_{\infty} - V_0)}{(V_{\infty} - V_t)}$

Five values of k are calculated and entered below:

- (i) $k = \dots\dots\dots \text{s}^{-1}$
 - (ii) $k = \dots\dots\dots \text{s}^{-1}$
 - (iii) $k = \dots\dots\dots \text{s}^{-1}$
 - (iv) $k = \dots\dots\dots \text{s}^{-1}$
 - (v) $k = \dots\dots\dots \text{s}^{-1}$
-
- Average $k = \dots\dots\dots \text{s}^{-1}$
-

k is calculated from $\log (V_{\infty} - V_t)$ against t plot (Graph IX) Using Eq. 15.29,
 $k = -2.303 \times \text{slope}$

= s⁻¹

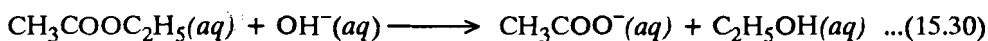
15.4.6 Result

- k (by calculation) = s⁻¹
- k (by graphical method) = s⁻¹

15.5 EXPERIMENT 20 : KINETICS OF SAPONIFICATION OF ESTER – TITRIMETRY

15.5.1 Principle

As mentioned earlier, the hydrolysis of ester is catalysed by acids and alkalies. The alkaline hydrolysis of ester is known as saponification. The equation for the saponification of ethyl acetate is given below:



Chemical Kinetics

Soaps are prepared by the alkaline hydrolysis of oils (which are esters of fatty acids of higher molecular weight). Hence alkaline hydrolysis of esters came to be known as saponification.

This reaction is irreversible, whereas the acid catalysed reaction is reversible. This reaction can be followed volumetrically by estimating the concentration of OH^- in the reaction mixture at different t values. The reaction mixture is prepared by mixing equal volumes of a solution of sodium hydroxide ($M/40$) and a solution of ethyl acetate ($M/40$) noting the time simultaneously. Then equal volumes of the reaction mixture are pipetted out at definite intervals into a known excess of cold standardised hydrochloric acid ($M/40$) and the left over acid back titrated with a standardised solution of sodium hydroxide ($M/40$). Pouring into excess hydrochloric acid solution neutralises the OH^- in the reaction mixture, thus quenching the reaction. As the reaction progresses, the concentration of OH^- in the reaction mixture decreases and the concentration of the unreacted hydrochloric acid in the quenched reaction mixture increases. The data that we collect is the volume of NaOH , V_t , required to react with the left over hydrochloric acid in the quenched reaction mixture at time t . Let us next see how we calculate k value from such a set of data.

The rate equation for the reaction can be written as:

$$-\frac{d[\text{OH}^-]}{dt} = k [\text{CH}_3\text{COOC}_2\text{H}_5][\text{OH}^-] \quad \dots (15.31)$$

The reaction is first order each in ethyl acetate and hydroxide ions. Assuming this, we are going to find the second order rate constant, k . Further, we take the ester and alkali of the same concentration initially (c_0) and assume that the concentration of each becomes $(c_0 - x)$ after a time t .

Then Eq. 15.31 can be written as,

$$-\frac{d[\text{OH}^-]}{dt} = (c_0 - x)^2 \quad \dots (15.32)$$

The generalised form of Eq. 15.33 is given in Table 13.1 of Unit 13 of this course.

On integration Eq. 15.31 becomes,

$$\frac{1}{c_0 - x} = \frac{1}{c_0} + kt \quad \dots (15.33)$$

Next let us see how to relate the titre value V_t of NaOH solution to $(c_0 - x)$.

Let us assume that 10 cm^3 of the reaction mixture is added to 25 cm^3 of $M/40$ HCl for quenching.

Volume of reaction mixture	=	10 cm^3
Volume of $M/40$ HCl added to it	=	25 cm^3
25 cm^3 of $M/40$ HCl	\equiv	25 cm^3 of $M/40$ NaOH

Volume of $M/40$ NaOH required for neutralisation of the excess hydrochloric acid

$$= V_t \text{ (say)}$$

Acid used for the neutralisation of unreacted NaOH in 10 cm^3 of the reaction mixture	}	$= (25 - V_t) \text{ cm}^3$ of $M/40$ NaOH
Concentration of unreacted NaOH in the reaction mixture		

$$= (c_0 - x) = \frac{(25 - V_t)}{10} \cdot \frac{M}{40} = \frac{(25 - V_t)}{400} M \quad \dots (15.34)$$

Since equal volumes of $M/40$ ester and $M/40$ alkali are mixed, initial concentration of $\text{NaOH} = c_0 = M/80 \quad \dots (15.35)$

Using Eqs. 15.33 to 15.35,

$$\frac{400}{(25 - V_t)} = 80 + kt \text{ (without mentioning units)} \quad \dots (15.36)$$

$$\text{or } k = \frac{1}{t} \left(\frac{400}{(25 - V_t)} = 80 \right) \dots (15.37)$$

Hence by substituting V_t at different time intervals, k can be calculated (using Eq. 15.37). Also by plotting $(400/(25 - V_t))$ against t , a straight line will be obtained, the slope being equal to k .

$$\text{Slope} = k \dots (15.38)$$

15.5.2 Requirements

Apparatus		Chemicals
Burette (50 cm ³)	- 1	Ethyl acetate
Pipettes (10 cm ³)	- 2	Sodium hydroxide
Beaker (250 cm ³)	- 1	Hydrochloric acid
Conical flask (250 cm ³)	- 1	Phenolphthalein
Conical flasks (100 cm ³)	- 2	Ice (from deionized water)
Water trough/Thermostat	- 1	
Thermometer	- 1	
Stopwatch	- 1	

Solutions that are provided:

1. *M*/40 ethyl acetate
2. *M*/40 NaOH
3. *M*/40 HCl
6. Phenolphthalein solution (for use as indicator)

Details for the preparation of the solution are given in Appendix.

15.5.3 Procedure

1. Bring to your work table all the required apparatus and solutions as given under Sec. 15.5.2.
2. Keep approximately 250 cm³ of *M*/40 HCl in ice for cooling.
3. Withdraw 50 cm³ of *M*/40 ester (from the burette kept commonly for the class) into a 250 cm³ conical flask.
4. Rinse and fill your burette with *M*/40 NaOH.
5. Withdraw from the burette 50 cm³ of *M*/40 NaOH into a 250 cm³ beaker and fill the burette again.
6. Keep the conical flask containing the ester solution and the beaker containing NaOH in a water trough (or thermostat) and note the temperature.
7. Start the reaction only after HCl (that has been kept for cooling) has reached a temperature near 5° C.
8. Start the reaction by pouring NaOH (in the beaker) into the ester solution (in the flask) and note the time simultaneously. Mix well by pouring from one into the other.
9. Pipette 25 cm³ of ice cold HCl into a 100 cm³ conical flask. Pipette 10 cm³ of the reaction mixture into this HCl, noting the time when the pipette is half empty. Add a drop of phenolphthalein and titrate with *M*/40 NaOH.
10. Repeat the sampling and titration at 5 minutes intervals initially and increase the intervals gradually to 20 minutes. Take in all 8 - 9 readings.
11. Enter the burette readings and time in Observation table VI.

100 cm³ of the reaction mixture contains

- (i) 50 cm³ of *M*/40 NaOH solution (in 250 cm³ beaker) and
- (ii) 50 cm³ of *M*/40 ester (in 250 cm³ conical flask)

15.5.4 Observation

Temperature of the reaction mixture = °C

V_t in Observation Table VI refers to the volume of $M/40$ NaOH required for neutralisation of excess acid.

Observation Table VI

t/s	Burette reading		$\frac{V_t}{\text{cm}^3}$
	Initial	Final	

15.5.5 Calculation

Five values of rate constants are calculated using Eq. 15.37 and their average is found out:

- (i) $k = \dots\dots\dots M^{-1} s^{-1}$
(ii) $k = \dots\dots\dots M^{-1} s^{-1}$
(iii) $k = \dots\dots\dots M^{-1} s^{-1}$
(iv) $k = \dots\dots\dots M^{-1} s^{-1}$
(v) $k = \dots\dots\dots M^{-1} s^{-1}$
Average $k = \dots\dots\dots M^{-1} s^{-1}$

A plot of $\frac{400}{(25-V_t)}$ against t (graph X) is made

As per Eq. 15.38, $k = \text{slope}$
 $= \dots\dots\dots M^{-1} s^{-1}$

15.5.6 Result

The rate constant for the saponification of ester (by titrimetry)

- (i) by calculation = $\dots\dots\dots M^{-1} s^{-1}$
(ii) by graphical method = $\dots\dots\dots M^{-1} s^{-1}$

15.5.7 Precaution

Ethyl acetate solution should be prepared the day it is to be used because slow hydrolysis reaction occurs even in the absence of OH^- ions.

15.6 EXPERIMENT 21 : KINETICS OF SAPONIFICATION OF ESTER – CONDUCTOMETRY

15.6.1 Principle

In the previous experiment, we followed the saponification of ester volumetrically by titrating the alkali remaining unreacted in the reaction mixture, as the reaction progresses. In this experiment, we will be following the same reaction by measuring the conductance of the reaction mixture. As the reaction progresses, OH^- ions are

replaced by acetate ions which have a much lower conductance (i.e.) ($\frac{1}{5}$ th that of OH^-). Consequently the conductance of the reaction mixture falls. The change in the conductance is approximately proportional to the amount of reaction that has taken place.

In this experiment, equal concentrations of the ester and alkali will be taken just as in the case of last experiment. We shall assume that the reaction is first order in each reactant and find out the second order rate constant. Thus Eqs. 15.30 to 15.33 hold good for this experiment also. We shall rewrite Eq. 15.33 for use in this experiment.

$$\frac{1}{(c_0 - x)} = \frac{1}{c_0} + kt \quad \dots (15.33)$$

Once we relate the conductance values to $(c_0 - x)$ and c_0 , we can calculate k . Let us first see the outline of the experiment.

The reaction mixture is prepared by mixing $M/40$ solution of ethyl acetate and $M/40$ solution of sodium hydroxide, noting the time simultaneously. Then the conductance values, G_t , of the reaction mixture are measured at definite time (t) intervals. If G_0 and G_∞ are the conductances of the reaction mixture at $t=0$ and at $t = \infty$ (end of the reaction) respectively, then

$$\begin{aligned} c_0 - x &\text{ is proportional to } (G_t - G_\infty) && \dots (15.39) \\ \text{and } c_0 &\text{ is proportional to } (G_0 - G_\infty) \end{aligned}$$

Introducing Q as the constant of proportionality, we write,

$$\begin{aligned} (c_0 - x) &= Q (G_t - G_\infty) && \dots (15.40) \\ \text{and } c_0 &= Q (G_0 - G_\infty) \end{aligned}$$

The value of Q can be obtained from Eq. 15.40 since c_0 and $(c_0 - x)$ (i.e., the concentration OH^- at the start of the reaction and after a time, t) as also G_t, G_0 and G_∞ are known.

Substituting for $[\text{OH}^-]$ in terms of conductance values from Eq. 15.40 into Eq. 15.33, we get,

$$\frac{1}{(G_t - G_\infty)} = \frac{1}{(G_0 - G_\infty)} + Qkt \quad \dots (15.41)$$

It is possible to calculate k using Eq. 15.41. In order to obtain k by graphical method, $1/(G_t - G_\infty)$ values are plotted against t . The rate constant, k , is obtained from the straight line plot.

$$\text{Slope} = Qk \quad k = \text{Slope}/Q \quad \dots (15.42)$$

15.6.2 Requirements

Apparatus		Chemicals
Conductometer	- 1	Ethyl acetate
Conductivity cell	- 1	Sodium hydroxide
Stopwatch	- 1	Acetic acid
Thermometer	- 1	Phenolphthalein
Pipette (50 cm ³)	- 1	Deionized water
Pipette (25 cm ³)	- 1	
Volumetric flasks (100 cm ³)	- 2	
Beakers (250 cm ³)	- 2	
water trough/Thermostat	- 1	
Wash bottle		

Chemical Kinetics

Details for the preparation of the solution are given in Appendix.

Solutions that are provided for the experiments(a) and (b):

1. $M/40$ ester solution
2. $M/40$ NaOH
3. $0.1 M$ acetic acid
4. Phenolphthalein indicator solution

15.6.3 Procedure

1. Bring to your work - table all the required apparatus and solutions as given under 15.6.2.
2. Prepare $M/80$ NaOH by pipetting 50 cm^3 of $M/40$ NaOH into a 100 cm^3 volumetric flask and making up to the mark with deionised water. Leave this flask in a water trough (or a thermostat).
3. Prepare $M/80$ sodium acetate by pipetting 50 cm^3 of $M/40$ NaOH into a 100 cm^3 volumetric flask. Add a drop of phenolphthalein and titrate this with $0.1 M$ acetic acid till the solution turns colour less. Then make up this solution to the mark with deionised water. Leave this flask too in the water trough (or thermostat).
4. During the time taken by the solutions of sodium hydroxide and sodium acetate to come to the temperature of the bath, get the solutions of ester and NaOH required for the kinetic run ready. Pipette 25 cm^3 of $M/40$ ester into a 250 cm^3 beaker. Then pipette 25 cm^3 of $M/40$ NaOH into another 250 cm^3 beaker. Allow these beakers to stand in a water trough (or a thermostat).
5. Connect the conductometer to the mains and to the conductivity cell. Switch on the conductometer keeping the mode selector at CAL. Set the range selector at 20. Adjust the sensitivity control to set the meter reading to mid scale. After this adjustment, do not disturb the sensitivity control.
6. Rinse and fill the conductivity cell with $M/80$ NaOH. Shift the mode selector to READ, note the conductance of the solution (G_0) and enter under observations.
7. Shift the mode selector to CAL. Rinse and fill the conductivity cell with $M/80$ sodium acetate. Shift the selector to READ, note the conductance (G_∞) and enter under observations. Shift to CAL.
8. Pour 25 cm^3 of $M/40$ NaOH in the beaker into the other beaker containing 25 cm^3 of $M/40$ ester solution, noting the time simultaneously. Mix the solutions well by pouring from one beaker to the other. Rinse and fill the conductivity cell with this reaction mixture.
9. Shift the knob to READ. Note the conductance of the reaction mixture at frequent time intervals. Take 12-15 readings of conductance (G_t) and time (t) and enter these in Table VII.

50 cm^3 of the reaction mixture contains

- (i) 25 cm^3 of $M/40$ ester (in a 250 cm^3 beaker) and
- (ii) 25 cm^3 of $M/40$ NaOH (in another beaker)

Note :

It is more convenient and accurate to read the time for certain conductance values than to read the conductance for certain time values. By this we can avoid making approximate estimates of conductance when the meter needle is in between two divisions. Read the time when the meter needle is against a division.

10. Note the temperature of the thermostat and enter under observations.

15.6.4 Observation

Temperature of the reaction mixture	= °C
Conductance of $M/80$ sodium hydroxide solution (G_0)	= mS
Conductance of $M/80$ sodium acetate solution (G_∞)	= mS

method of following reactions obeying zeroth order, first order and second order kinetics. The preparation of solutions used in Experiments 17–21 is discussed in the next section.

15.8 APPENDIX

Preparation of Solutions for Experiments 17(a) – (c) and 18 :

- 0.05 M I₂ in 0.4 M KI (approximately) :
Weigh 12.7 g of iodine and place this in a 250 cm³ beaker. Add to the beaker, 66.4 g of KI and approximately 40 cm³ of deionised water. Stir to dissolve all the iodine and, transfer the solution to a 1 dm³ volumetric flask and make up to the mark with deionised water.
- 2 M HCl (approximately) :
Transfer in small lots 180 cm³ of concentrated hydrochloric acid (11 M) using a measuring cylinder to a 1 dm³ volumetric flask which contains approximately 500 cm³ of deionised water. Shake the flask after the addition of each lot. Make up to the mark with deionised water. Let us call this solution by the name, hydrochloric acid (A). To know the molarity of solution (A) exactly, let us dilute the solution by 20 times (10 cm³ of A diluted to 200 cm³). Let this be called solution (B). Let us titrate solution (B) against 0.1 M sodium carbonate solution using methyl orange indicator. If the molarity of hydrochloric acid (B) is *p*, then the molarity of hydrochloric acid (A) is 20 *p*.
- 1 M HCl :
To prepare 1 M HCl (accurately) from hydrochloric acid (A), the following procedure is adopted. Transfer (1000/20 *p* =) 50/*p* cm³ of hydrochloric acid (A) into a 1 dm³ standard flask and make up to the mark with deionised water. The resultant solution is 1 M HCl.
- 0.10 M NaHCO₃ (approximately) :
Weigh 33.6 g NaHCO₃ and transfer to a 5 dm³ bottle or jar. Add 4 dm³ of deionised water in small lots, dissolve NaHCO₃ and shake the solution well. As this solution is used only for quenching, the molarity need not be exact. Hence one can make this solution in any big bottle (5 dm³) or plastic jar. One need not look for a volumetric flask.
- 0.01 M Na₂S₂O₃ (approximately) :
Weigh 4.96 g of Na₂S₂O₃·5H₂O and transfer to a 2 dm³ volumetric flask. Dissolve and make up to the mark with deionised water. Prepare this solution on the day the experiment is to be done. Standardise this solution with standard K₂Cr₂O₇ titrimetrically.
- 1% starch solution :
Heat about 900 cm³ of deionised water in a beaker. Then make a paste of 10 g of soluble starch and 100 cm³ of deionised water. Pour this gradually with stirring into the boiling water and, continue boiling for a few minutes. Then cool the solution. Starch solution should always be prepared just before use.
- Acetone :
Acetone is to be used as such for Experiments 17(a) - (c). But, for Experiment 18, 4 M acetone is to be used. The preparation of 4 M acetone is done as follows:
Using a burette, transfer 73.5 cm³ of acetone into a 250 cm³ flask and, make up the solution to mark with deionised water.

Preparation of Solutions for Experiment 19 :

For this experiment, the concentration of the following solutions need not be known exactly.

For the purpose of standardisation of HCl solution (B), 250 cm³ of sodium carbonate solution is prepared by weighing accurately about 1.325 g sodium carbonate, dissolving in minimum quantity of water and making up to the mark in a 250 cm³ standard flask.

For the purpose of standardisation of sodium thiosulphate, 0.01 M K₂Cr₂O₇ (about 0.7356 g solid K₂Cr₂O₇ weighed accurately, dissolved and made up to 250 cm³) is prepared. 20 cm³ of standard K₂Cr₂O₇ solution is treated with 10 cm³ of 10% KI solution and the liberated iodine is titrated using sodium thiosulphate solution prepared above. The titration is carried out till straw yellow coloured solution is obtained, whereby a few drops of 1% starch solution is added. A blue colour develops due to starch-iodine complex and the titration is conducted till the blue colour disappears leaving a green coloured solution. From the titre values, the molarity of sodium thiosulphate can be calculated.

1. 0.5 M HCl :
Transfer 45 cm³ of concentrated hydrochloric acid (11 M) using a measuring cylinder to a 1 dm³ volumetric flask which contains approximately 500 cm³ of deionised water. Shake the flask after the addition of each lot. Make up to the mark with deionised water.
2. 0.125 M NaOH :
Dissolve 10 g sodium hydroxide pellets in 2 dm³ of deionised water kept in a 5 dm³ jar.
3. Phenolphthalein indicator solution :
Dissolve 5 g of phenolphthalein in 500 cm³ of ethanol. Add 500 cm³ of water stirring it constantly. Filter the solution, if there are any solid particles.

Preparation of Solutions for Experiments 20 & 21

1. M/40 CH₃COOC₂H₅ :

Pipette 4.9 cm³ of ethyl acetate into a 2 dm³ flask containing some deionised water and then make up to the mark with deionised water. This solution should be prepared on the day it is to be used because a slow reaction takes place even in the absence of OH⁻ ions.

If you want to prepare a more exact solution of ester, then adopt the following procedure. This method also reduces error due to the volatalisation of the ester. Take a clean dry weighing bottle and weigh it with some deionised water. Pipette 4.9 cm³ of the ester into the weighing bottle and weigh it again. Transfer the ester solution carefully into a 2 dm³ volumetric flask, repeatedly wash the weighing bottle with deionised water and transfer the washings also into the standard flask. Finally make up the solution to the mark.

$$\text{The molarity of ester} = \frac{\text{Mass of ester}}{\text{Molar mass} \times \text{Volume of solution in dm}^3 \text{ of ester}}$$

If 4.9 cm³ of ester is made up to 2 dm³ in a standard flask, the molarity of ester can be calculated knowing that density of ester is 0.90 g/cm³ and its molar mass is 88 g/mol.

$$\begin{aligned} \text{Molarity of ester} &= \frac{\text{Mass of ester}}{\text{Molar mass} \times \text{Volume of the solution in dm}^3} \\ &= \frac{4.9 \times 0.9}{88 \times 2} M = 0.025 M \end{aligned}$$

2. 0.1 M NaOH (approximately) :
Prepare an approximately 0.1 M NaOH solution by dissolving 8 g (weighed approximately on a rough balance) of sodium hydroxide pellets and dissolving in 2 dm³ of deionised water. The exact strength of this solution is found by titrating against a standard solution of potassium hydrogen phthalate. Let the molarity of this solution be *p*.
3. M/40 NaOH :
To prepare M/40 NaOH solution, (2000/40*p* cm³ =) 50/*p* cm³ of sodium hydroxide solution of molarity *p* prepared above, is taken in a 2 dm³ standard flask, made up to the mark with deionised water and shaken well. The resultant solution is M/40 NaOH.
4. M/40 HCl :
Transfer 4.5 cm³ of concentrated HCl (11 M) using a measuring cylinder to a 2 dm³ volumetric flask which contains approximately 1 dm³ deionised water and shake the flask. Make up to the mark with deionised water. Standardise this acid using M/40 NaOH solution prepared above and phenolphthalein indicator.
5. Phenolphthalein indicator solution :
This is to be prepared as given in Experiment 19.
6. 0.1 M acetic acid :
Using a burette, transfer 7.5 cm³ of glacial acetic acid into a 250 cm³ volumetric flask containing 100 cm³ of water and make up the solution to the mark. This solution (say, acetic acid (A)) is approximately 0.5 M. 20 cm³ of this solution is diluted to 100 cm³ in a standard flask to obtain acetic acid

For the purpose of standardisation of NaOH solution, 0.1 M potassium hydrogen phthalate is prepared by weighing accurately about 5.105 g potassium hydrogen phthalate (molecular weight : 204.2), dissolving it in water and making up to 250 cm³. Phenolphthalein is to be used as indicator for the titration between potassium hydrogen phthalate and sodium hydroxide. From the titre values, the molarity of sodium hydroxide solution (say, *p*) is calculated.

Chemical Kinetics

(B). The molarity of acetic acid (B) is found out by titrating against standardised p molar solution of sodium hydroxide prepared above using phenolphthalein indicator. If the molarity of acetic acid (B) is y , then the molarity of acetic acid (A) is $5y$.

To prepare 250 cm^3 of 0.1 M acetic acid, $(250 \times 0.1/5y =) 5/y \text{ cm}^3$ of acetic acid (A) is diluted to 250 cm^3 in a standard flask.