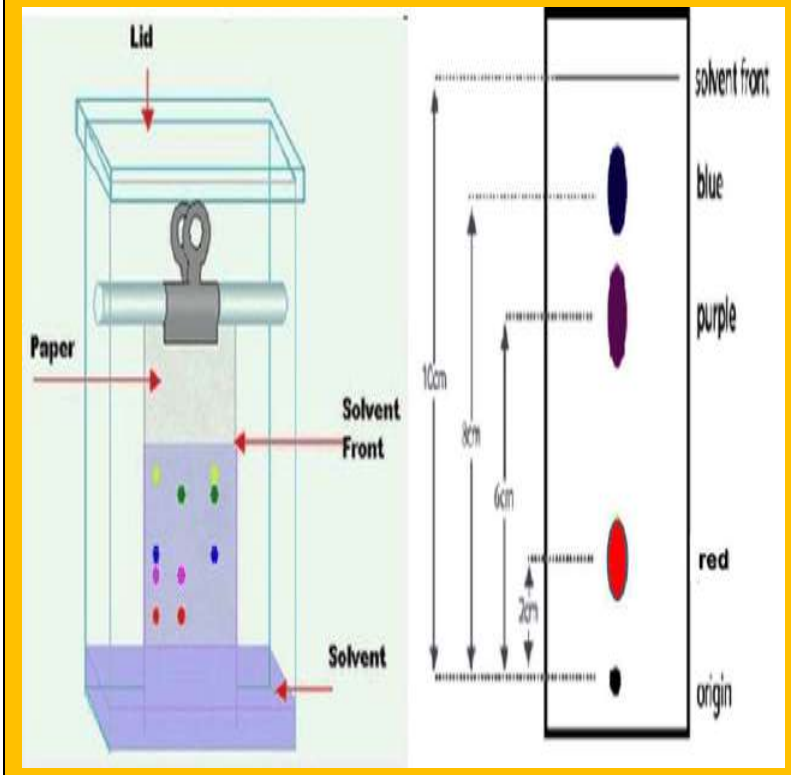
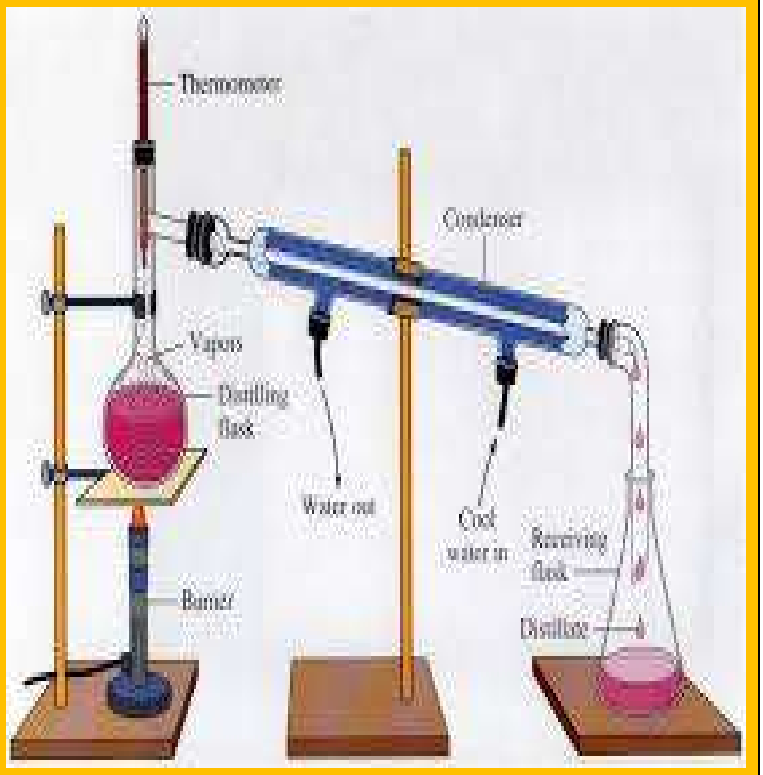
MSCCH-510 L
M.Sc II Semester
Laboratory Course -II





SCHOOL OF SCIENCE
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY,HALDWANI (NAINITAL)

MSCCH-510 L

Laboratory Course -II

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CONTENTS

BLOCK I: PHYSICAL CHEMISTRY

UNIT 1: KINETIC STUDIES

CONTENTS :

1.1 INTRODUCTION

Chemical Kinetics is a branch in physical chemistry which deals with the study of a chemical reaction, the factors affecting their rates the mechanism by which a chemical reaction occurs.

According to chemical kinetics, chemical reactions can be classified into three types;

- **Fast / Instantaneous Reactions:**
  Chemical reaction which completes in less than 10-12 second is known as fast reaction. The rate of reactions is very fast e.g. Acid – base reactions, precipitation reactions, organic substitution reactions etc.
- **Extremely Slow Reactions:**
  In some processes the rate of the reaction is extremely slow. Reaction takes a long time from some minutes to years e.g. rusting of iron, biological ageing transformation of diamond and all the natural processes.
- **Moderately Slow Reactions:**
  Reactions proceeding with measurable rates are moderately slow reactions. These reactions take time intermediate between slow and fast reaction e.g. inversion of sugarcane and hydrolysis of esters, etc.

Rate of reaction (Average and instantaneous rate)

Rate is usually expressed as the ratio of the amount of change in some quantity to the time required to produce the change

$$\text{Rate} = \frac{\text{Change in some quantity}}{\text{Time taken for the change}} = \frac{\Delta x}{\Delta t}$$

The term Δx means $x_{final} - x_{initial}$ and Δt is the amount of the elapsed.

The rate measured over a long time interval is called average rate and the rate measured for infinitesimally small interval is called instantaneous rate.

Rate Constant

Consider a simple reaction,

$$A \rightarrow B$$

If C_A is the molar concentration or active mass of A reactant at a particular instant, then

$$\frac{dx}{dt} \propto C_A \text{ or } \frac{dx}{dt} = k\, C_A$$

Where k is called velocity constant or rate constant.

Factors influencing rate of reaction: There are a number of factors which influence the rate of the reaction. Some of the major factors are;

- **Nature of the reactants:** The nature of the reacting species plays an important role in influencing the rates of the reaction. The rate of reaction depends upon the:

(a) Physical state of the reactant

(b) Size of the reactant

(C) Chemical nature of the reactant

- **Concentration of the reactant:** It has been observed that the rate of reaction decreases with passage of time. As the reaction proceeds, the concentration of the reactant decreases. Thus, the rate of the reaction is directly proportional to the concentration of the reactant.
- **Temperature:**

The rate of reaction increases considerably with increase in temperature. The rate of many reactions approximately doubles or triples for every 10°C rise in temperature.

- **Catalyst:**

In the presence of the catalyst, the reaction follows a path of lower activation energy. The lower the activation energy, higher will be the rate of reaction.

Molecularity of a reaction:

It is defined as 'the minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of the reactions'. For example, molecularity of inversion of cane sugar and decomposition of dibromosuccinic acid will be two and one, respectively.

$$C_{12}H_{22}O_{11} + H_2O \rightleftharpoons C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_4H_4O_4Br_2 \rightleftharpoons C_4H_3O_4Br + HBr$$

Reactions having molecularity of one, two, three etc. are known as unimolecular reactions, bimolecular reactions and tri molecular reactions etc. respectively.

Order of Reaction

Reactions are classified not only on the basis of their molecularity but also accordingly to the order of the reaction, which is defined as the **'***Sum of the powers to which the concentration terms of the reactants must be raised in order to determine the rate of the reaction'***.**

- **Zero Order Reactions :**

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e. the rate is proportional to the zeroth power of the concentration of the reactants.

$$A \rightarrow \text{Products}$$

For a zero order reaction

$$-\frac{dx}{dt} = k\,[A]^0$$

- **First Order Reactions :**

A reaction is said to be first order if its rate is determined by the change of one concentration term

$$A \rightarrow \text{Products}$$

Let 'a' be the concentration of A at the start and after time t, the concentration becomes (a-x), i.e. x has been changed into products. The rate of reaction after time 't' is given by the expression

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

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

Separating the variables, integrating the above equation and using the fact that when t= 0, x = 0, we have

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

- **Second order Reaction:**

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

When the concentration of both reactants is equal or two molecule of the same reactant are involved in the change, i.e.

$$A + B \rightarrow \text{Products}$$

$$2A \rightarrow \text{products}$$

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

On solving this equation

$$k = \frac{1}{t} \cdot \frac{x}{(a-x)}$$

Where a = initial concentration of the reactants and x = concentration of the reactant changed in time t.

(ii) When the initial concentration of the two reactants are different, i.e.

$$A + B = \text{Products}$$

Initial concentration a b

Then rate $\frac{dx}{dt} = k\,(a-x)\,(b-x)$

$$k = \frac{2.303}{t(a-x)}\log_{10}\frac{b(a-x)}{a(b-x)}$$

(a-x) and (b-x) are the concentration of A and B after time interval, t.

Reactions involving four or more molecules are very rare. The chances of simultaneous collision of reacting molecules will go on decreasing with increase in the number of molecules. Thus the possibility of three molecules colliding together is much less than in the case of bimolecular collision. The possibility of four molecules colliding together is much less than in case of tri-molecular reactions. Hence, high molecularity reactions are rare.

Determination of the Order of the Reaction:

The important methods used for determining the order of reactions are given below:

I. Graphical Method:

A graphical method based on the respective rate laws can also be used.

If the plot of log (a-x) versus 't' is a straight line, the reaction follows first order.

If the plot of 1/ (a-x) versus 't' is a straight line, the reaction follows second order order.

If the plot $1/ (a-x)^2$ versus 't' is a straight line , the reaction follows third order.

In general, for a reaction of n^{th} order, a graph of $1/ (a-x)^{n-1}$ versus t must be a straight line.

II. Methods of integration (Hit and trial method):

The most simple method is the one in which the quantities, x and t are determined and substituted in the kinetic equation of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of the reaction. If all the reactants are at the same molar concentration, the kinetic equations are:

$$K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}, \text{ for the first order reactions;}$$

$$K = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right], \text{ for the second order reactions;}$$

$$K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right], \text{ for third order reactions;}$$

III. Isolation Method

This method was given by Ostwald in1902. In this method, the concentration of all reactants except one is taken in large excess and the order of the reaction is then determined by any method with respect to that reactant (which is not taken in excess). Then in another separate experiment, the concentration of any other reactant is not taken in excess, while of all others is taken in excess. The order of reaction is again determined. The experiment is repeated by isolating each reactant in turn, the total order of reaction will be the sum of the order of all isolated reaction.

Consider the reaction

$$n_1 A + n_2 B + n_3 C \rightarrow \text{Products}$$

In this n_1 number of moles of A, n_2 number of moles of B, n_3 number of moles of C etc. are reacting, the reaction velocity is given as follows;

$$\frac{dx}{dt} = k\, c_A^{n1}.c_B^{n2}.c_C^{n3}$$

In one experiment, the reactant B and C are taken in large excess and the order of reaction determined with respect to A. Suppose it is n_1. Then in another experiment, reactants A and C are taken in large excess and the order of the reaction with respect to B is determined as above. Let it be n_2. Similarly, let the order of a reaction with respect to C, taking A and B in large excess be n_3. Then the total order of the reaction is given by $n = n_1 + n_2 + n_3$.

IV. Van't Hoff differential method:

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction. Thus, for two different initial concentrations C_1 and C_2, equation can be written in the form

$$-\frac{dc_1}{dt} = kC_1^n \text{ and } -\frac{dc_2}{dt} = kC_2^n$$

Taking logarithms

$$\log_{10}\left(-\frac{dc_1}{dt}\right) = \log_{10}k + n\log_{10}C_1 \qquad \ldots\ldots\ldots\ldots (1)$$

and $$\log_{10}\left(-\frac{dc_2}{dt}\right) = \log_{10}k + n\log_{10}C_2 \qquad \ldots\ldots\ldots\ldots(2)$$

Subtracting Equation (2) from (1)

$$\log_{10}\left(-\frac{dc_1}{dt}\right) - \log_{10}\left(-\frac{dc_2}{dt}\right) = n\,(\log_{10}C_1 - \log_{10}C_2)$$

$$n = \frac{\log_{10}\left(-\frac{dc_1}{dt}\right) - \log_{10}\left(-\frac{dc_2}{dt}\right)}{(\log_{10}C_1 - \log_{10}C_2)}$$

$-\frac{dc_1}{dt}$ and $-\frac{dc_1}{dt}$ are determined from concentration vs time graph and the value of 'n'can be determined.

V. Half life method:

A general expression for the half life, $(t_{1/2})$, is given by

$$(t_{1/2})\ \alpha\ \frac{1}{a_1^{n-1}}$$

Where 'n' is the order of the reaction.

Starting with different initial concentration a_1 and a_2 for the same reaction, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively are determined. As we know,

$$(t_{1/2})_1 \alpha \frac{1}{a_1^{n-1}} \quad \text{.....(3)}$$

&

$$(t_{1/2})_2 \alpha \frac{1}{a_2^{n-1}} \text{..... (4)}$$

Dividing (3) by (4)

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \quad \text{..... (5)}$$

Taking logarithms on both sides,

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)[\log_{10}a_2 - \log_{10}a_1]$$

$$(n-1) = \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{\log_{10}a_2 - \log_{10}a_1}$$

$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{\log_{10}a_2 - \log_{10}a_1} \text{.....(6)}$$

Above relation can be used to determine order of the reaction.

The temperature coefficient (Activation Energy):

Increase in temperature in almost all cases increases the velocity of a reaction to a marked extent. It has been seen that in general the specific rate becomes approximately double or triple for an increases in temperature by 10°C. The ratio of specific rate at temperature separated by 10°C usually 25°C and 35°C is called the temperature coefficient of the reaction rate. Thus

$$\text{Temperature coefficient} = \frac{k_{(t+10)}}{k_t} = 2 \text{ to } 3 \text{..... (7)}$$

Where k_t is the specific rate at t°C and $k_{(t+10)}$ at 10°C.

The above method is approximate for indication of the influence of the temperature as the coefficient decreases with increasing temperature. The variation of rate constant is best expressed in the form of an exponential equation known as Arrhenius equation

$$k = Ae^{-Ea/RT} \quad \text{.....} \quad (8)$$

Where E_a is the energy of activation (J mol^{-1}) and A is a constant, known as Arrhenius frequency factor. Taking logarithm of above equation, we have

$$\ln k = \ln(Ae\text{-}Ea/RT)$$

Solving the equation further: $\ln k = \ln(A) + \ln(e\text{-}Ea/RT)$

$$\ln k = \ln(A) + (-Ea/RT)$$

$$\ln k = \ln(A) - \frac{E_a}{RT}\left(\frac{1}{T}\right)$$

If k_1 and k_2 are specific rates at two temperature T_1 and T_2 then,

$$\ln \frac{k2}{k1} = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Thus, the measurements of specific rates of a reaction of two temperatures enable E_a to be calculated. E_a also calculated by plotting a graph between log k and 1/T. The straight line will be obtained, slope of this line equal to $-E_a/2.303$.

1.2 OBJECTIVE

This unit will be helpful in:

- Understanding chemical kinetics experiment.
- Understanding the rate of a reaction and rate laws
- Studying the effect of factors which influence the rate of a reaction, such as temperature, pressure, concentration and catalyst.
- In knowing the mechanism of the sequence of steps by which a reaction occurs.

The knowledge of the rate of reactions is very valuable in understanding the chemistry of reactions. It is also of great importance in selecting optimum conditions for an industrial process so that it proceeds at a rate to give maximum yield.

1.3 DETERMINATION OF THE VELOCITY CONSTANT OF AN ACID CATALYZED HYDROLYSIS OF ESTER.

1.3.1. Object

To determine the velocity constant of an acid, say HCl catalyzed hydrolysis of methyl acetate at laboratory temperature.

1.3.2. Requirements

Methyl acetate, HCl solution (1M/2M), NaOH solution (0.5M), Ice cold water, pipette, burette, conical flask, conical flask with stopper (Erlenmeyer flask), Phenolphthalein (indicator), measuring cylinder, 150ml & 250ml beaker, distilled water.

1.3.3 Theory

Hydrolysis of an ester in aqueous medium is very slow. Hence, the reaction rate is in enhanced by an acid (HCl). The reaction is as given as follows

$$CH_3COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3COOH + CH_3OH$$

Methyl acetate — Acetic Acid — Methanol

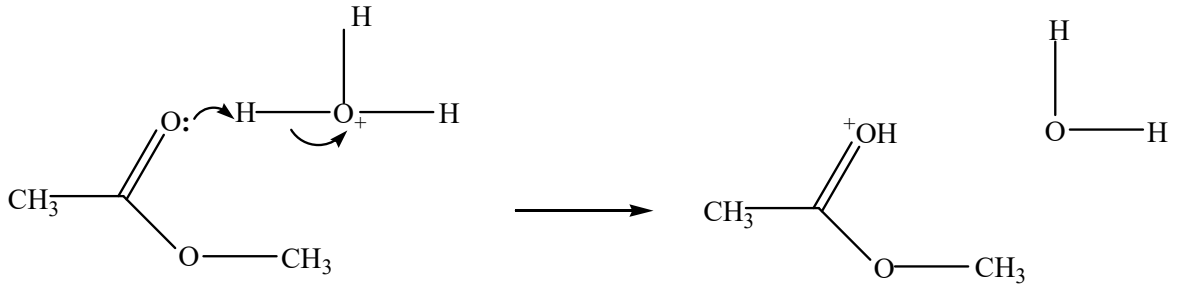
$$\text{Rate} = K'[CH_3COOCH_3][H_2O]$$

$$\text{Rate} = K[CH_3COOCH_3]^1 \quad (\text{where } K = K'[H_2O])$$

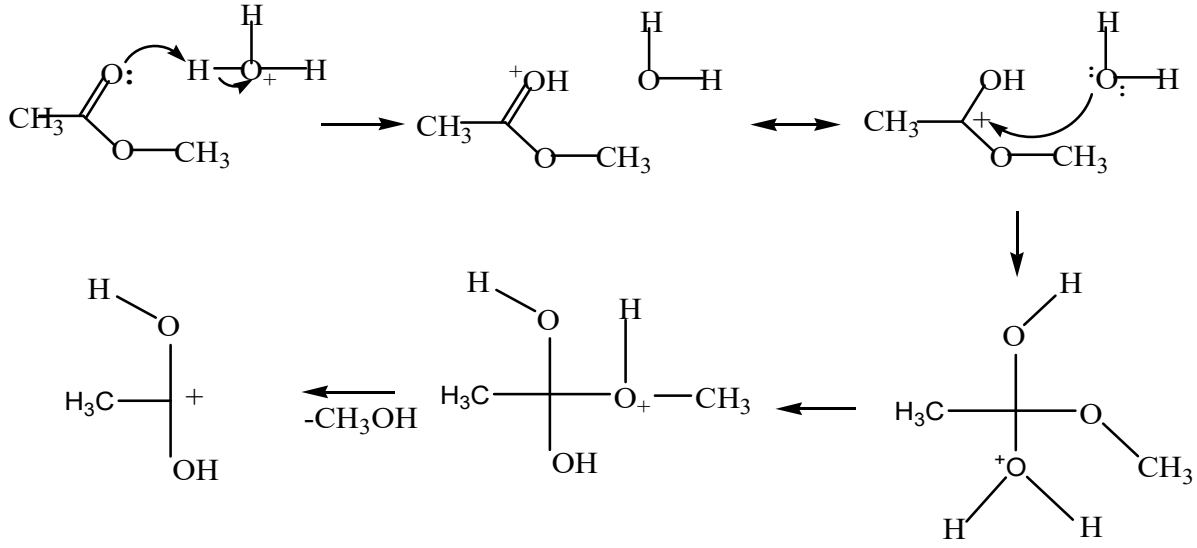
K= Pseudo first order rate constant

The reaction is of 1st order with respect to methyl acetate. Since water is present in large excess, therefore, its concentration remains practically constant throughout the reaction. So the reaction is referred to as a pseudo first order reaction.

The actual catalyst in this reaction is the hydroxonium ion ($H^+ + H_2O \rightarrow H_3O^+$), present in all solution of acids in water. In the first step, the ester takes a proton from the H_3O^+ ion. The proton becomes attached to one of the lone pairs on the oxygen which is double bonded to the carbon.

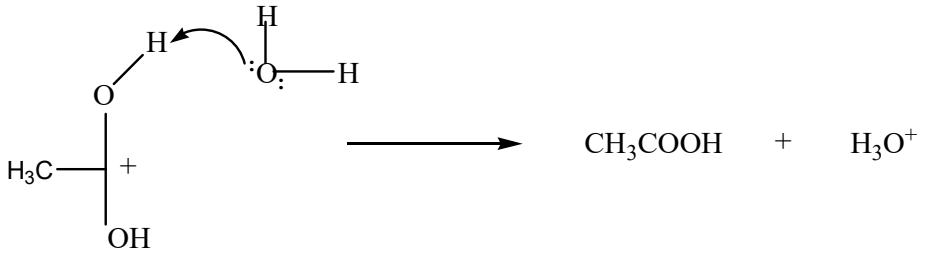


The transfer of the proton to the oxygen gives it a positive charge, but the charge is actually delocalized. The positive charge on the carbon atom is attacked by one of the lone pairs on the oxygen of a water molecule.



Proton gets transferred from bottom oxygen atom to one of the others. Now a molecule of

methanol is lost from the ion. i.e. one of the products of the reaction. The hydrogen ion is removed from the oxygen by reaction with a water molecule. Other product of the reaction acetic acid is produced and the catalyst H_3O^+ ion is regenerated.



Rate Constant:

$$k = \frac{2.303}{t}\log\left[\frac{V_\infty - V_0}{V_\infty - V_t}\right]$$

1.3.4. Procedure

Take 100 ml of 1M HCl solution in clean reagent bottle and fill the burette with N/5 NaOH solution. Now add 10 ml of pure methyl acetate to the reagent bottle containing HCl and shake the solution gently. Quickly pipette out 10 ml of the reaction mixture into a clean conical flask containing ice cold water in order to quench the reaction. Now add 2 to 3 drops of phenolphthalein as indicator and titrate against 0.5 M NaOH solution and end point of the titration should be taken at the appearance of the pink colour. Note down the titre value in the tabular form as V_t and repeat the same titration procedure for every 10 minutes of regular intervals of time (for one hour). Tabulate the titre value as V_t.

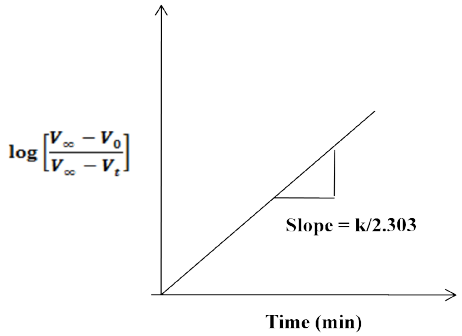
For V_∞: Heat the remaining reaction mixture for half an hour by maintaining 50-60℃ temperature. Cool it to room temperature under tap water. Pipette out 10 ml of the reaction mixture into a clean conical flask and titrate against NaOH solution using phenolphthalein as an indicator and the titre value V_∞ is obtained.

Experimental Graph: Plot a graph between log $[(V_\infty - V_0)/ [(V_\infty - V_t)]$ V_s against time, straight line passing through origin is obtained. From the slope the velocity constant or rate constant can be calculated. Plot another graph between log $(V_\infty - V_t)$ against time, a straight line with negative slope is obtained.

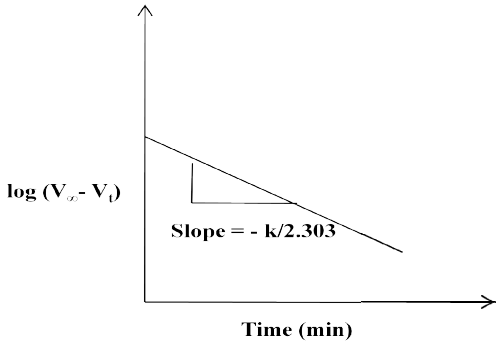
The amount of acetic acid formed at the end of the experiment is equivalent to the initial amount of methyl acetate and V_0, V_t ,V_∞ are the volumes of N/5 NaOH solution used at zero, t and ∞ time respectively. The amount of acetic acid produced after time 't' i.e. value of 'x' is directly proportional to $V_t - V_0$. The initial concentration of methyl acetate i.e. value of 'a' is directly proportional to $V_\infty - V_0$. Therefore, the count of ester present at time 't' i.e.

$$(a-x) \alpha (V_\infty - V_0) - (V_t - V_0)$$

which implies that $(a-x) \alpha (V_\infty - V_t)$



Graph 1



Graph 2

Observation Table:

S. No.	Time (min)	Volume of N/5 NaOH	(V_∞- V_t)	log (V_∞- V_t)	[(V_∞- V_0)/ [(V_∞- V_t)]	log [(V_∞- V_0)/ [(V_∞- V_t)]	K= 2.303/t log [(V_∞- V_0)/ [(V_∞- V_t)]
1	0	V_0	V_∞- V_0=				
2	10	V_{10}	V_∞- V_{10}=				
3	20	V_{20}	V_∞- V_{20}=				
4	30	V_{30}	V_∞- V_{30}=				
5	40	V_{40}	V_∞- V_{40}=				
6	50	V_{50}	V_∞- V_{50}=				
7	60	V_{60}	V_∞- V_{60}=				
8	70	V_{70}	V_∞- V_{70}=				
9	80	V_{80}	V_∞- V_{80}=				
10	V_∞		-				

Average Value of k =

1.3.5. Result

Velocity Constant (k) for the studied reaction is ……..min^{-1}

1.3.6. Precautions

1. The reactants must be allowed to attain temperature of the thermostat or bath.
2. The mean time of mixing should be taken as starting point of the reaction, i.e. zero time.
3. Conical flasks used for titration should be steam washed.

1.4 *EFFECT OF TEMPERATURE, DETERMINATION OF ACTIVATION ENERGY (VALIDITY OF ARRHENIUS EQUATION) AND FREQUENCY FACTOR OF A REACTION.*

1.4.1. Object

To verify the effect of temperature, determine activation energy (validity of Arrhenius Equation) and frequency factor of a reaction by kinetic studies.

1.4.2. Requirements

Iodination flask, burette, pipette, standard flask, conical flask, beaker, measuring jar, thermostat, stop watch, 0.1 M KI, 0.05 K_2SO_4, M/ 200 hypo, starch indicator.

1.4.3. Theory

$$S_2O_8 + 2I^- \rightarrow I_2 + 2SO_4^{-2}$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

With increase in temperature, there is an increase frequency of the collision due to more 'energetic' situation, but this is the minor factor when considering why rate of reaction increase with temperature. The minimum energy required for the reaction; the activation energy, stays the same on the increasing temperature. However, the average increase in particle kinetic energy caused by the absorbed heat means that much greater proportion of the reactant molecule now has the minimum or activation energy to react. At higher temperature, there are more particles with the higher kinetic energies.

Arrhenius suggested that the variation of rate constant with temperature can be expressed as:

$$k = A\, e^{-Ea/RT}$$

Where A is known as the frequency factor or pre-exponential factor, e is the base of the natural logarithm system, E_a is the activation energy in joules/mole, R= 8.31J K mol is the ideal gas law constant and T is the temperature in Kelvin. Generally the rate of reaction is doubled or tripled for every 10 ^{0}C rise in temperature. Exponential equation like the Arrhenius equation produce curved lines when plotted. It is desirable to convert equation into that of straight line, because then the activation energy and the pre exponential factor can be found. The way to convert an exponential equation into a straight line equation is to take the natural logarithm of both sides.

$$\ln k = \frac{E_a}{RT} + \ln A$$

$$y = m\,x + b$$

If the natural logarithm of k is plotted versus the reciprocal of temperature (1/T), a straight line is produced. The slope, m of the line, is then the negative activation energy divided by the ideal gas constant and the y intercept is b, is the natural logarithm of the pre-exponential factor.

1.4.4. Procedure

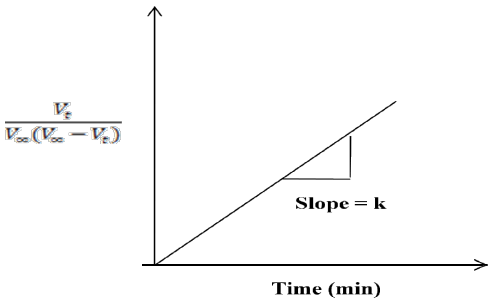
Prepare all the required solutions. Pour 50ml M $K_2S_2O_8$ and 50 ml of 0.1 KI in 250 ml iodination/ standard flask separately. Keep the flask in thermostat and maintain the temperature at 30^{0}C. Fill

the burette with hypo. Keep a conical flask ready for titration with some ice coldwater. Now add above contents and note down the time, After 10 minutes pipette out 10 ml of reaction mixture into a conical flask containing ice cold water and add few drop of freshly prepared starch solution. The solution turns blue. The end point is indicated by the disappearance of blue colour. Note down the titre value and repeat the similar procedure at regular time intervals 20, 30,……. minutes respectively.

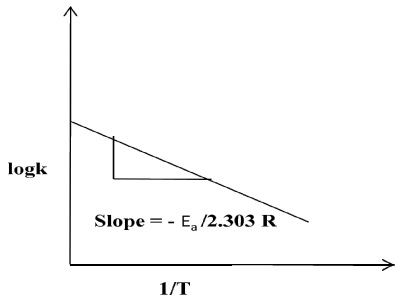
For V_∞: At early stage of the reaction i.e. after 2 to 3 minute, pipette out 10 ml of the reaction mixture into a clean conical flask and excess of KI to it. Cover it with watch glass and keep it in dark for about 30 minute. After 30 minutes, take out the flask and wash the lid of watch glass into the conical flask. Titrate the content of the conical flak against hypo and note down the reading as V_∞. Repeat the similar experiment procedure for 35^0C, 40^0C, 45^0C, 50^0C and 10-15^0C.

Model Graph:

Plot of graph between [$V_t/(V_\infty - V_t)$] and Time (min) (Graph 1) for each set, it gives straight line passing through origin, the slope of the line is equal to second order rate constant (k) for the reaction.



Graph 1



Graph 2

According to Arrhenius, Plot a graph between log k vs (1/T), a straight line is obtained. From slope and intercept of this graph, E_a and A can be calculated (Graph 2).

1.4.5. Observations

Set	Temp(K)	K (Rate constant) lit.mole^{-1},min^{-1}		
1	303	Calculation	Graph1	Graph2
2	308			
3	313			
4	318			
5	323			

From the slope and intercept, determine the activation energy (kJ/mol) and frequency factor of the reaction.

1.4.6. Result:

1.5 DETERMINATION OF THE EFFECT OF CHANGE IN CONCENTRATION OF THE REACTANTS ON RATE CONSTANT OF A REACTION.

1.5(a).1. Object

To determine the effect of change in concentration of the reactants on the rate constant of a reaction by initial rate method.

1.5(a) .2. Requirements

Iodination flask, burette, pipette, conical flask, beaker, measuring jar, stopwatch, 0.1 M solution of KI, 0.05 K_2SO_4, M/200 hypo, starch indicator.

1.5(a).3. Theory

$$S_2O_8^{-2} + 2I^- \rightarrow I_2 + 2SO_4^{-2}$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

The rate law for the above reaction is expressed Rate $= K\,[I^-]^m\,[S_2O_8^{-2}]^n$

The rate of a chemical reaction is a measure of how quickly reactants are consumed or products are formed during a chemical reaction. The rate is the change in the reactant or product concentration divided by the change it time. The rate depends upon several factors including the concentration of reactant. Since reactants concentration decrease as the reaction proceeds, reaction rates also decreases the reaction proceeds- i.e. the reaction rate does not remain the constant during the reaction. The reaction rate will be different depending upon which time interval we consider. The rate of the reaction is greatest at the beginning of the reaction and is very low towards at the end. The average rate is the change in reactant or product concentration divided by the change in time. The larger the period of time over which an average rate is measured, the more the rate change over that time period. Thus, it is common to make the time period as short as possible. The shorter the time period, the less the rate will change during the period. If the time period is made infinitesimally short, then the rate is called an instantaneous rate. The instantaneous rate at the very beginning of the reaction when the time= 0 is called the initial rate.

In this experiment, concentration of KI remains constant. Thus the order 'n' can be determined by altering the initial concentration of persulphate and the rate expression is thus modified as

$$\text{Rate} = K\,[S_2O_8^{-2}]^n$$

$$\log(\text{Rate}) = \log K + n \log [S_2O_8^{-2}]$$

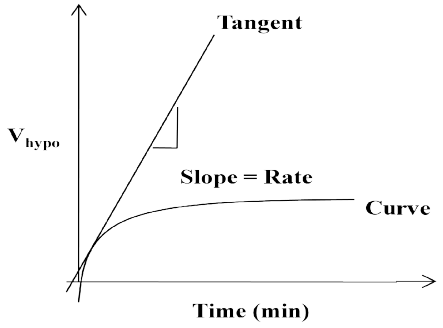
1.5(a).4. Procedure

Prepare the 0.1 M solution KI, 0.05 M $K_2S_2O_8$, 0.05 M K_2SO_4 and M/200 hypo and prepare the following sets of mixtures.

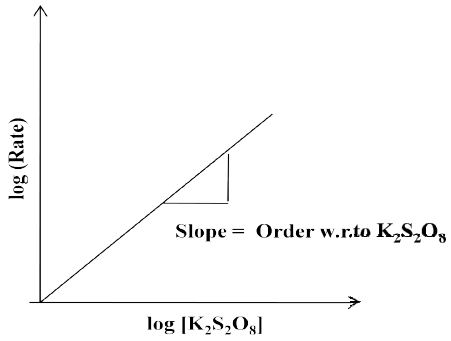
Sets	I	II	III	IV	V
Volume of KI (mL)	25	25	25	25	25
Volume of $K_2S_2O_8$ (mL)	25	20	15	10	05
Volume of K_2SO_4 (mL)	0	05	10	15	20

Pipette out 10 ml of the reaction mixture after 5 min from the first set and pour into the conical flask, which already containing ice cold water. Add few drops of starch indicator to it and titrate against the hypo. Repeat the same process for 10, 15, 20….. minutes and note down the burette readings at the above mentioned regular intervals and repeat the same experimental procedure for all the sets given in above table. Calculate the solution concentration of $K_2S_2O_8$ for each set.

Experimental Graph: Plot a graph between volume of hypo (ml) required vs time (min) for each set, it gives a curve or straight line, the slope of the line is equal to rate for the reaction. Plot another graph between log [Rate] vs log [$K_2S_2O_8$], a straight line with positive slope and intercept is obtained. The slope of the line equals to order with respect to $K_2S_2O_8$.



Graph 1



Graph 2

1.5(a).5. Observations

Table -2 (for all Sets)		
S. No.	Time (min)	Volume of Hypo (ml)
1	5	
2	10	
3	15	
4	20	
5	25	

Table -3				
Set	Rate	log [Rate]	[$K_2S_2O_8$]	log [$K_2S_2O_8$]
I				

II				
III				
IV				
V				

1.5(a).6. Result

Order of the reaction with respect to $K_2S_2O_8$ (by initial rate method) = ……..

1.5 (b).1.Object

To determine the effect of change in concentration of the reactants on rate constant of a reaction by isolation method.

1.5 (b).2. Requirements

Iodination flask, burette, pipette, conical flask, beaker, measuring jar, stopwatch, 0.25 M solution of KI, 0.025 M K_2SO_4, 0.25 M KCl, M/200 hypo, starch indicator.

1.5 (b).3. Theory

$$\mathbf{S_2O_8^{-2} + 2I^- \rightarrow I_2 + 2SO_4^{-2}}$$

$$\mathbf{2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6}$$

The rate law for the above reaction is expressed Rate = $K\,[I^-]^m\,[S_2O_8^{-2}]^n$

The isolation method is a technique for simplifying the rate law in order to determine its dependence on the concentration of a single reactant. Once a rate law has been simplified, the differential or integral methods may be used to determine the reaction orders. The dependence of the reaction rate on the chosen reactant concentration is isolated, so that all other reactants present remain essentially constant through the course of the reaction.

In this experiment concentration of the KI is taken in excess and $K_2S_2O_8$ remains constant.

Thus, the order 'm' can be determined by altering the concentration of the iodide and the rate expression is thus modified as

$$\text{Rate} = k\,[I^-]^m$$

$$\log(\text{rate}) = \log k + m \log [I^-]$$

1.5 (b). 4. Procedure :

Prepare 0.25 KI solutions, 0.025 M $K_2S_2O_8$, 0.25 M KCl, M/200 hypo and prepare the following sets of mixture

Sets	I	II	III	IV	V
Volume of KI (ml)	25	20	15	10	05

Volume of $K_2S_2O_8$ (ml)	25	25	25	25	25
Volume of KCl (ml)	0	05	10	15	20

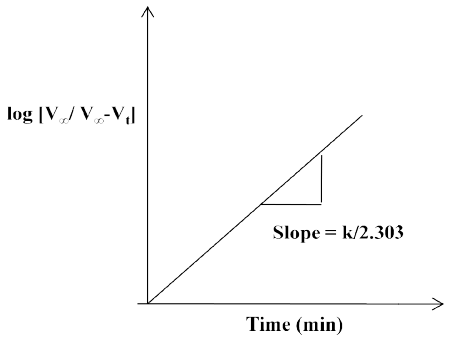
Pipette out 10 ml of the reaction mixture after 5 min from the first set and pour into the conical flask, which already containing ice cold water. Add a few drops of starch indicator to it and titrate against the hypo. Repeat the same process for 10, 15, 20,…….. minutes and note down the burette reading for the all 't' above mentioned regular intervals and repeat the similar experiment procedure for the sets which is given in the above table. Calculate the rate (pseudo first order) constant for obtained data and solution concentration of KI for each set.

Observations

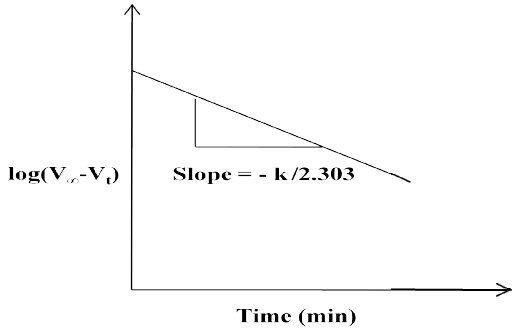
Time (min)	Volume of hypo required (mL)	$(V_\infty - V_t)$	$\log (V_\infty - V_t)$	$[V_\infty / V_\infty - V_t]$	$\log [V_\infty / V_\infty - V_t]$	K
5						
10						
15						
20						
25						
30						
∞	V_∞ =					

Where $k = \frac{2.303}{t} \log \left[\frac{V_\infty}{(V_\infty - V_t}\right]$

Experimental Graph: Plot a graph between $\log [V_\infty / V_\infty - V_t]$ vs time for each set, it gives a straight line passing through origin, the slope of the line is equal to the k/2.303, from this rate constant can be calculated. Plot another graph between $\log (V_\infty - V_t)$ vs time, a straight line with negative slope and intercept is obtained.



Graph 1



Graph 2

1.5 (b).5.Result:

Set	K (Rate constant) min^{-1}

	Calculations	Graph 1	Graph 2
I			
II			
III			
IV			
V			

1.6 DETERMINATION OF THE EFFECT OF CHANGE IN CONCENTRATION OF THE CATALYST ON RATE CONSTANT OF A REACTION.

1.6. (a).1 Object

To study the effect of change in concentration of the catalyst on reaction rate by following the kinetics of CH_3 CO CH_3 –I_2 reaction.

1.6 (a).2 Requirements

Volumetric flask, pipettes, burette, stopwatch, thermostat, acetone, 0.01 M iodine solution in 10 % KI solution, 1M sodium acetate or 0.05 M $NaHCO_3$ solution, standard 0.01 M hypo solution, 0.5 M H_2SO_4, Starch solution.

1.6 (a).3. Theory

Iodine reacts with acetone in the presence of an acid (catalyst) according to the reaction:

$$CH_3CO\,CH_3\,(aq) + I_2 \xrightarrow{H^+} CH_3COCH_2I\,(aq) + H^+(aq) + I^-$$

If acetone is taken in large excess, its concentration may be taken to be constant. Therefore, the rate of reaction is seen to be independent of iodine concentration, i. e. the reaction rate is of zero order with respect to iodine, i.e.

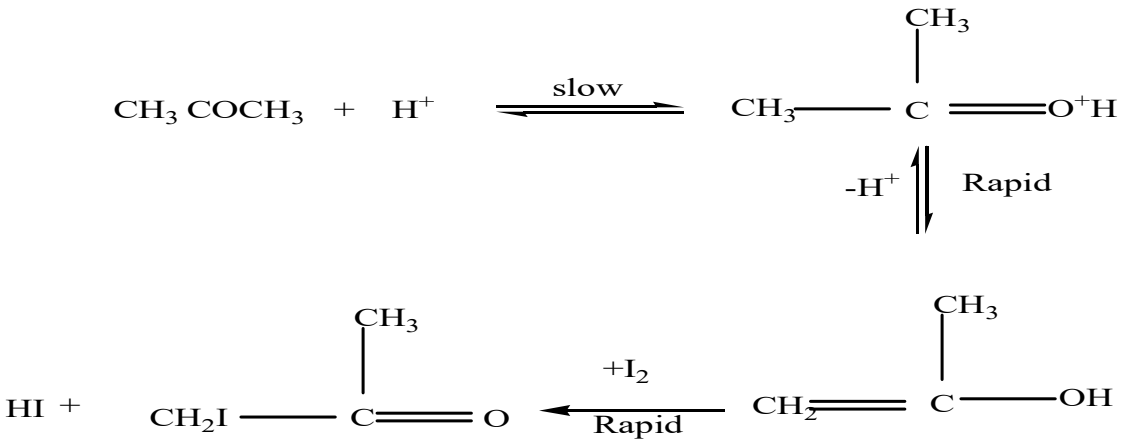
$$-\frac{d[I_2]}{dt} = k'[I_2] = k$$

$$-d[I_2] = kdt$$

$$[I_2] = -kt + C$$

The reaction is, however, followed by withdrawing samples from the reaction mixture at different intervals of time and titrating it with sodium thio sulphate solution.

As the reaction is of zero order with respect to iodine, therefore, the rate determine step does not involve the interaction between ketone and iodine molecule. The mechanism suggested is as follows;



As the enolisation of acetone is the slowest reaction, hence it determines the rate of the reaction.

1.6 (a).4. Procedure:

In a conical flask, place 10 ml 0.5 M H_2SO_4 and 60 ml of distilled water and thermostat the flask at 25 ℃. In a separate flask suspended in thermostat place about 50 ml I_2 solutions. After the solutions have attained the equilibrium temperature, pipette out 10 ml of 0.1M solution into the acetone flask. Start the stop watch when the pipette is half discharged.

After mixing the solutions, withdraw 10 ml of the solution mixture in a conical flask and add 20 ml of N- sodium acetate solution and check the reaction. The reaction can also be checked by adding $NaHCO_3$ free from Na_2CO_3. Titrate the reaction mixture with 0.01 M sodium thiosulphate solution, using starch solution as a indicator. The titre value gives the amount of residual iodine in the sample. Withdraw 10 ml of the reaction mixture after an interval of 5 minutes and proceed, as explained above.

Repeat the above process with varying amounts of acetone, iodine and acid to study the effect of the change in their concentration. Prepare the following mixture:

Bottle number	**Acetone (ml)**	**M/2 H_2SO_4**	**N/10 I_2 solution (ml)**	**Water (ml)**
1	10	20	10	60
2	10	20	05	65
3	05	20	10	65
4	10	10	10	70

Observations:

Bottle 1		Bottle 2		Bottle 3		Bottle 4	
Time (mts)	**Volume of hypo (ml)**	**Time (mts)**	**Volume of hypo (ml)**	**Time (mts)**	**Volume of hypo (ml)**	**Time (mts)**	**Volume of hypo (ml)**

Calculations:

Plot a curve between titre values as ordinate and time as abscissa for all the four bottles bottles and find the slope of each curve. The slope will give the value of the velocity constant. i.e. k. the straight line graph shows the reaction to be zero order with respect to iodine.

From the value of rate constants for bottle 1 and 2 sets, calculate the order of the reaction with respect to acetone as follows:

When acetone and acid are taken in large excess,

$$\frac{d[I_2]}{dt} = k_1\,[I_2]^x$$

Where $$k_1 = k\,[\text{Acetone}]_1^y\,[\text{Acid}]^z \quad \ldots\ldots\ldots\ldots (1)$$

When acetone concentration is halved the new value of k_1 is given by

$$k_1' = k\,[\text{Acetone}]_2^y\,[\text{Acid}]^z \quad \ldots\ldots\ldots\ldots\ldots (2)$$

From equation 1 and 2

$$\frac{k_1}{K_1'} = \left\{\frac{[\text{Acetone}]_1}{[\text{Acetone}]_2}\right\} = (2)^y$$

Now calculate the value of the y. Similarly, from the values k for bottles 1 and 4, calculate the value of z, i.e. order with respect to the acid used as catalyst.

1.6 (a).5. Result: The reaction is of zero order with respect to iodine.

1.6 (b).1. Object

To determine the effect of Mn^{+2} on rates of reaction between oxalic acid and $KMnO_4$ in acidic medium

1.6 (b).2.. Requirements

Iodination flask, burette, pipette, conical flask, beaker, measuring jar, stop watch, 0.1 M KI solution, 0.2M $H_2C_2O_4$, 0.2 Mn Cl_2, M/100 hypo, 0.02M$KMnO_4$, 2M H_2 SO_4, Starch indicator.

1.6 (b). 3. Theory

Autocatalytic reactions are those in which at least one of the products is a reactant. The key feature of these rate equations is that they are non linear. The graph for these reactions is a sigmoid curve, which is a typical for autocatalytic reactions. These chemical reactions proceed slowly at the start and rate of the reaction increases progressively. This is due to amount of catalyst increase the reaction as the reaction proceeds and then it again slows down as the reactant concentration decreases. If the concentration of a reactant or product in an experiment as follows

a sigmoid curve, the reaction may be autocatalytic. Per magnate in acidic solution can oxidize oxalate ion (oxalic acid). The reaction produces Mn^{+2}, The chemical reaction is given as follows

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

It is an example of auto catalytic reaction. This reaction is catalyzed by Mn^{+2} ions. When acidified potassium permanganate undergoes a reaction with oxalate solution, the rate of the reaction is initially slow. It slowly increases the rate of the reaction due to the formation of Mn^{+2} ions. If a little amount of Mn^{+2} is added to the reactants initially, the reaction proceeds at a fast rate right from the beginning. If that is not done, the rate of the reaction follows a sigmoid curve with more Mn^{+2} being created as one of the products.

Mechanism:

$KMnO_4$ is a well known oxidizing agent, in acidic medium it oxidized the oxalate ions and itself undergo reduction to Mn^{+2}

$$MnO_4^- + 8H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O \quad \times \text{ two}$$

$$2C_2O_4^- \rightarrow 2CO_2 + 2e^- \quad \times \text{ five}$$

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

If a small amount of Mn^{+2} is added, it act as a homogeneous catalyst because it easily oxidizes to Mn^{+2} by MnO_4^- ion and then reduced back to Mn^{+2} by $C_2O_4^{2-}$ ion.

$$MnO_4^- + 8H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$$

$$Mn^{2+} \rightarrow Mn^{3+} + e^- \quad \times \text{ five}$$

$$MnO_4^- + 8H^+ + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4\,H_2O \quad \times \text{ two}$$

$$2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2 \quad \times \text{ five}$$

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

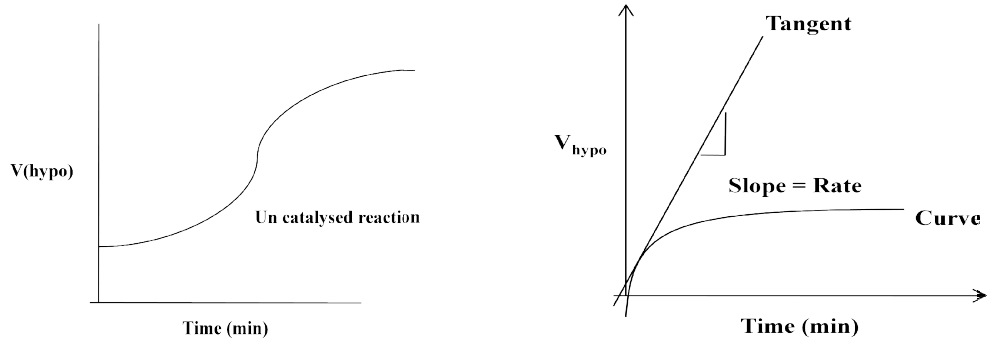
1.6 (b).4. Procedure: 0.1 MKI solution, 0.2 M $H_2C_2O_4$ solution, 0.2 $MnCl_2$, 0.02 M $KMnO_4$, 2M H_2SO_4 and prepare the following set of mixtures:

Experiment/Set	$H_2C_2O_4$ (ml)	H_2SO_4 (ml)	Mn^{2+}(ml)	H_2O (ml)	$KMnO_4$ [last](ml)
I	50	2.5	0	0	25

II	50	2.5	5	42.5	25
III	50	2.5	10	37.5	25
IV	50	2.5	15	32.5	25

Solution of KI, $H_2C_2O_4$, $MnCl_2$, H_2SO_4 & $KMnO_4$ pour in a separate beakers and place the beaker in water bath to obtain thermal equilibrium. Kinetics run may be started when thermal equilibrium with bath has been reached. Pipette out10 ml of the reaction mixture after 5 min from the first set into the conical flask and add about 10 ml of 0.1 M KI solutions. This reacts with remaining amount of $KMnO_4$ and stops further reaction. Titrate the librated iodine with M/100 hypo solution using starch indicator. Repeat the same process for 10.15.20….. minutes and note down the burette reading at above mentioned regular intervals and repeat the similar procedure for all the sets mentioned in the above tabular form.

Experimental Graph: Plot a graph between volumes of hypo required vs time (min) for each set. It gives a sigmoid curve for un catalyzed reaction and gives a curve or straight line for catalyzed reaction, the slope of the line equal to rate for the reaction.



1.6 (b).5. Result

The plot of volume of hypo required vs time gives a sigmoid curve for un-catalyzed (set 10 reaction, it indicates that the reaction is auto catalyst. For catalyzed reactions (set-2, 3,4), the rate of reaction increases with increase in concentration on Mn^{+2}.

1.7. DETERMINATION OF THE EFFECT OF CHANGE IN IONIC STRENGTH ON RATE CONSTANT OF A REACTION.

1.7.1. Object

To determine the effect of ionic strength on rate of $K_2S_2O_8$-KI reaction.

1.7.2. Requirements

Iodination flask, burette, pipette, standard flask, conical flask, beaker, 0.1 M KI solution, 0.05 M $K_2S_2O_8$, 0.1 M KCl, M/200 hypo, starch indicator

1.7.3. Theory

$$S_2O_8 + 2I^- \rightarrow I_2 + 2SO_4^{-2}$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

when reaction involving ionic species occur in a solution, addition of salt (KCl) can speed up the reaction as compared to when no salt is added. In those cases where there is an effect, it becomes greater as the concentration of added salt is increased. Theses salt effects can be understood qualitatively and quantitatively using an equation called the Bronsted- Bjerrum equation, named after those physical chemists instrumental in its discovery. In calculating the ionic strength, contribution from all ions present in solution must be included, including those from reactant and products. However, when the studies of the primary kinetic salt effect on reaction rate constant are made in practice, the concentration of the added salt is usually made high enough so that the contributions from reactants and products to the ionic strength can be neglected.

The relationship between the rate constant and the ionic strength (μ=I) is given by the following equation

$$\log k = 1.018 Z_A Z_B \sqrt{\mu} + \log \ (\mu=I)$$

Where k is dependent on the temperature. Z_A, Z_B are charges on A and B ions. μ is the ionic strength and it equal to ½ $n_i \sum C_i Z_i^2$.in ionic strength of a solution influence the reaction rate according to the sign of charge on the reacting substance A and B represented by Z_A and Z_B. If both the charges are negative or if both are positive, log k will increase. If both the reacting species have opposite sign, then log k decreases as √μ increases. In the present experiment, the reaction between two ionic species is given by,

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{-2}$$

Hence both ions have negative sign. We observe log k increases as √μ increases.

1.7.4. Procedure

Prepare 0.1 M solution of KI, 0.05 M $K_2S_2O_8$, 0.1 M KCl and M/200 hypo and prepare the following sets of mixture

Table: Sets for the effect of ionic strength on reaction rate

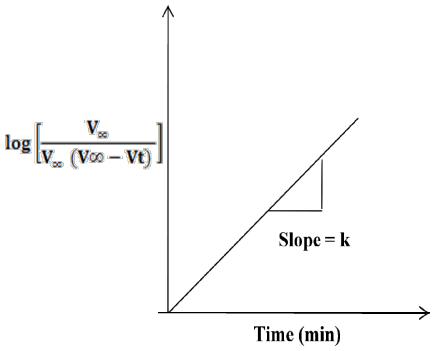
Sets	I	II	III	IV	V
Volume of KI(ml)	20	20	20	20	20
Volume of $K_2S_2O_8$ (ml)	20	20	20	20	20
Volume of KCl (ml)	0	05	10	20	30
Volume of H_2O (ml)	30	20	10	05	0

Pipette out 10 ml of the reaction mixture after 10 min from the first set and pour into the conical flask, which already containing ice cold water. Add few drops of starch indicator to it and titrate against the hypo. Repeat the same procedure for 20, 30, 40, …….. minutes and note down the burette reading at above mentioned regular intervals and repeat the same procedure for the sets given in the tabular form.

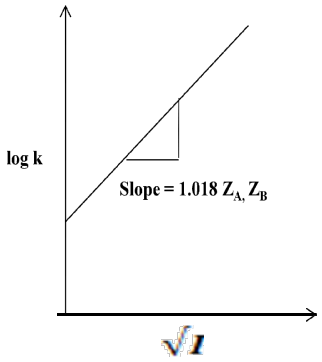
From the obtaining data calculate the second order rate constant and ionic strength of KCl for each set of reaction mixture.

Experimental Graph: Plot a graph between $1/(V_\infty - V_t)$ vs time (min) (Graph 1) for each set of, it gives straight line with positive slope and intercept, the slope of the line is equal to the second order rate constant for the reaction.

Plot another graph between log [rate constant] vs square root of Ionic strength of KCl for each set, gives the straight line, slope of the line is equal to the 1.018 Z_A, Z_B (Graph 2)



Graph 1



Graph 2

Table:

Set	K	log k	Ionic strength(I)	$\sqrt{I}$
I				
II				
III				
IV				
V				

1.7.5. Result

Rate of ($S_2O_8^{-2}$ and I^-) reaction increases with increase of ionic strength.

1.8 DERMINATION OF THE RATE CONSTANT FOR THE OXIDATION OF IODIDE IONS BY HYDROGEN PEROXIDE.

1.8.1. Object

To determine the rate constant for the oxidation of iodide ions by hydrogen peroxide using initial rate method

1.8.2. Requirements

Burette, pipette, conical flask, iodination flask, beakers, 0.1 M KI solution, 0.1 M H_2O_2, M/100 hypo, starch indicator, 0.25M HCl or H_2SO_4.

1.8.3. Theory

When H_2O_2 is added to a solution of KI, the iodide ions are slowly oxidized to iodine under acidic conditions , the reaction us given as follows

$$2I^- + 2H^+ + 2H_2O \rightarrow I_2 + 2H_2O$$

Progress of the reaction is monitoring by titrating the librated iodine with hypo solution using starch indicator.

$$I^- + H^+ + H_2O_2 \xrightarrow{\text{Slow}} HOI + H_2O$$

$$HOI + H_2O_2 \xrightarrow{\text{Fast}} I^- + H + H_2O + O_2$$

$$I^- + H^+ + HOI \longrightarrow I_2 + H_2O$$

$$I_2 + I^- \longrightarrow I_3^-$$

The rate law for this reaction should include the concentration of iodide, H^+ ions and H_2O_2.

$$\text{Rate} = K\,[I^-]^m\,[H_2O_2]^n\,[H^+]^p$$

If the concentration of H+ is held constant throughout the experiment then its effect will not appear in the rate law

$$\text{Rate} = K'\,[I^-]^m\,[H_2O_2]^n$$

The rate law for the reaction between iodide ions and H_2O_2 can be determining by carrying out experiments in which the concentration of iodide and H_2O_2 are varied. Using the initial rate, the order of the reaction can be determine as follows

Between two experiment the concentration of H_2O_2 remain constant while the ratio of the concentration of KI is 2:1.

$$\text{Rate 1} = K'\,[I^-]^m\,[H_2O_2]^n$$

$$\text{Rate 2} = K'\,[I^-]^m\,[H_2O_2]^n$$

$$= \text{Rate1/ Rate 2} = 2^m$$

From this m can be calculated, between another set of experiment the concentration of KI remain constant with the ratio of the concentration of H_2O_2 is 2:1

Rate 1 = $k' [I^-]^m [H_2O_2]^n$

Rate 3 = $k' [I^-]^m [H_2O_2]^n$

=Rate1/ Rate 3= 2^n

From this, n can be calculated.

The value of the rate constant k' can be determine by substituting the m and n value and the formula given as follows

$k' = Rate/ [KI]^m [H_2O_2]^n$

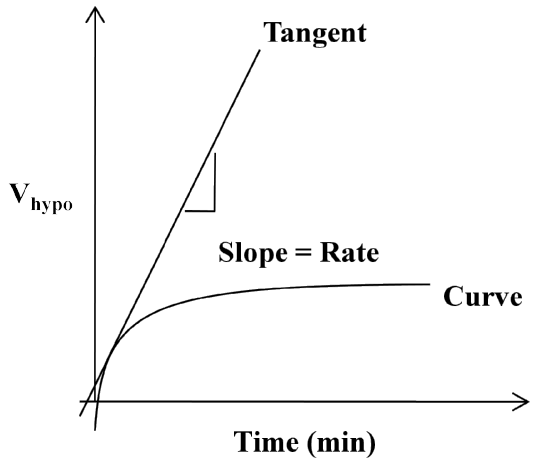
1.8.4. Procedure

Prepare 0.1 M KI solution, 0.1 M H_2O_2 Solution, 0.25 M HCl or H_2SO_4 and prepare the following sets mixtures. Solution of KI, HCl and H_2O_2 pour in separate beakers and place the beakers in a water bath to obtain thermal equilibrium. Kinetics run may be started when thermal equilibrium with bath has been reached. Pipette out 10 ml of reaction mixture after 5 min from the first set and pour into the conical flask, which already containing ice cold water. Add few drops of starch indicator to it and titrate against the hypo. Repeat the same process for 10, 15, 20…..minutes and note down the burette readings at above mentioned regular intervals. And repeat the similar experimental procedure for all the (3) set mentioned in the below tabular form.

Observation Table. Sets for determination of order with respect to KI and H_2O_2

Experiment/Set	KI (mL)	HCl (mL)	Water (mL)	H_2O_2 last (mL)
I	50	10	0	50
II	25	10	25	50
III	50	10	25	25

Experimental Graph: plot of graph between volume of hypo (ml) required vs time (min) for the each set, it gives a curve or straight line, the slope of the line is equal to rate for the reaction.



1.8.5. Result

Order of the reaction with respect to KI (m) =……

Order of the reaction with respect to H_2O_2 (n) =……..

Order of the reaction with respect to KI (m+n) =……

Experiment/Set	In solution concentration of KI	In solution of concentration of H_2O_2	Rate	k’
I				
II				
III				

1.9 TERMINAL QUESTIONS

Q.- 1. Mention any two factors which influence the rate of reaction

Q.- 2. What is the SI Unit of rate of reaction?

Q.- 3. Define rate constant of a reaction.

Q.- 4. Define order of a reaction.

Q.- 5. The conversion of molecules X to Y follows second order kinetics. If conc. of X Increased to three times, how will it affect the rate of formation of Y?

Q.- 6. Define pseudo first order reaction.

Q.- 7. How does rate of reaction vary with temperature?

Q.- 8.Write Arrhenius equation which relates the rate constant , activation energy and temperature.

Q.- 9. How is activation energy related to rate of reaction?

Q.- 10. How is activation energy calculated by plotting graph ln K against 1/T ?

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BLOCK I: PHYSICAL CHEMISTRY

UNIT 2: SURFACE CHEMISTRY

CONTENTS

2.1 INTRODUCTION

There are several examples which reveal the fact that the surface of a solid (or liquid) has the tendency to attract and retain the molecules of other immiscible phase with which it is brought into contact. These molecules remains only at the surface and do not go deeper into the bulk. The concentration of the molecular species is more at the surface than in the bulk of solid or liquid. This tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed as adsorption. The molecular species or substance which concentrates or accumulated at the surface is termed as adsorbate and the material on whose surface the concentration has taken place is called adsorbent. Since colloids have very small dimensions, they have very high surface area per unit mass, hence they are good adsorbents. Other adsorbents are silica gel, charcoal, clay etc.

Substance like iodine, which is soluble in water as well as carbon tetra chloride, though water and carbon tetra chloride are themselves immiscible. Thus when a solution of iodine in water is mixed or shaken with carbon tetra chloride, iodine distribute itself in such a way that at equilibrium the concentration of iodine in the two layers at any given temperature is constant. This is known as distribution law or partition law and is given by the equation

$$K = \frac{C_1}{C_2}$$

Where C_1 and C_2 are the concentration of the solute (iodine) in the two miscible liquids when equilibrium is reached and K, a constant, is the distribution or partition coefficient. The above equation holds true when the molecular state of the solute in the two liquids remains the same. But when the chemical changes like association, dissociation, salvation and complex formation takes place then deviation from the law occurs and complication may arises.

Molecules within the body of a liquid experience equal molecular attraction from all sides and as a resultant force is zero. At the surface, however, a molecule is surrounded by liquid molecule on one side and vapours on the other. Thus due to the difference in the number of molecule per unit volume of the liquid and vapour phase, the molecule experiences attraction inwards, towards the body of the liquid, at right angle to the surface. Due to such inward pull the surface of the liquid tends to contract to a minimum surface area and that is why the molecule at the surface experiences constant tension. This force causing strain to the molecules of the liquid at the surface is called 'Surface Tension'. It is defined as force in dyens acting at right angles to the surface of the liquid, one centimeter in length drawn in the surface. It is usually represented by symbol γ (gamma).

Due to tension on the surface, the liquids try to occupy the least area and that is why the drops of liquids are spherical. This is because in a sphere the surface area is minimum for a given volume. The rise of a liquid in a capillary is also due to surface tension. When the temperature increases, surface tensions will decreases.

Surface tension of liquid can be determined by a number of methods, these are following

I) Capillary rise method
II) Ring detachment method
III) Maximum bubble pressure method
IV) Drop weight and drop number method.

Above these methods, the drop weight and drop number method is most convenient and is commonly employed for relative determinations.

2.2 OBJECTIVE

By studying this unit, the students will be able to understand:

- Validity of Freundlich adsorption Isotherm
- How to determine the partition coefficients, molecular surface energy and association factor of liquids.

2.3 FLOWING CLOCK REACTIONS

2.3.1(a). Object

To determine the kinetics of iodine clock reaction.

2.3.1(b). Requirements

Solution A= 250 ml of 0.01 potassium persulphate, **Solution B**= 250 ml of 0.3 M KI + 0.0005M $Na_2S_2O_3$ + Starch solution, 10 ml in 250 ml of mixed solution. Thermostat, white glazed tile, beaker, measuring flask, pipette, thermometer, stop watch.

2.3.1(c). Theory

The reaction involves the oxidation of iodide ions to iodine by persulphate ions. The reaction can be monitored by sodium thiosulphate solution and starch solution can be used as an indicator to time the reaction.

2.3.1(d). Procedure

Place both the solutions in a bath of water at constant temperature and swirl them from time to time (for nearly 20-25 minutes) till they attain the temperature of the bath. Check the temperature by means of a thermometer. Pipette out 25 ml of solution A in a dry 100ml beaker, Rinse and drain a second 100 ml beaker with solution B and pipette out 25 ml of this solution into it. Pour solution B into solution A and start the stop watch. Mix the solution and put the beaker on a white glazed tile if water bath is not used. Record the time when the blue colour first appears.

Repeat the mixing of standard solution and note the time again for getting a concordant result.

Repeat the experiment by changing the concentration of $K_2S_2O_8$ solution as follows:

Bottle No.	Volume of Solution A (ml)	Volume of Solution B (ml)	Volume of water (ml)
1	25	25	0
2	20	25	5
3	15	25	10
4	10	25	15

If the temperature is maintained 20°C, the expected time for appearance of blue colour will be nearly 44, 56, 74, 110 seconds, respectively. Use the initial rate method for analyzing the experimental data.Repeat the experiment with double concentration of KI and $Na_2S_2O_3$ and interpret the results.

2.3.2.(a) Object:

To determine the Kinetics of bromination of Phenol by bromide –bromate mixture in an acid medium as a clock reaction.

2.3.2.(b) Requirements:

Pipettes, measuring Flask, Beakers, Burettes, Stop watch, white glazed tile, 0.005 M$KBrO_3$, 0.01 M KBr, 0.001 M phenol, 1 M H_2SO_4, Methyl orange solution as indicator.

2.3.2.(c).Theory:

The clock reaction of bromination of phenol by bromide-bromate mixture consists of the following steps

$$Br^- + BrO_3^- + 6H^+ = 3H_2O + 3Br_2 \text{ (Main Reaction)}$$

$$3Br_2 + C_6H_5OH = Br_3C_6H_5OH + 3H^+ + 3Br^-$$

$$Br_2 + \text{Methyl Orange} = \text{Colourless product (indicator reaction)}$$

The study involves the changing concentration of Br-, BrO_3^- and H+ ions.

Procedure:

I) Change of Initial Rate with Br- ion concentration

Immediately before starting the experiment, dilute the phenol solution with distilled water by making 5 ml of solution to 100 ml in measuring flask. Thus, 5×10^{-5} M phenol solution (A) is obtained. Dilute 40 ml of 1 M H_2SO_4 and 2 ml of methyl orange to 100 ml in another measuring flask (B). Using two 100 ml beakers, perform the

following five or more observations. Before mixing the solution, they are kept in a thermostat.

The time for disappearance of colour will be found to be inversely proportional to volume of KBr solution.

Beaker 1			Beaker2			Time (sec)
S.No.	KBr Solution (ml)	Water (ml)	$KBrO_3$ Solution (ml)	H_2SO_4 solution (B) (ml)	Phenol solution (A) (ml)	
1	10	0	10	15	1	t_1
2	8	2	10	15	1	t_2
3	6	4	10	15	1	t_3
4	5	5	10	15	1	t_4
5	4	6	10	15	1	t_5

[II] Change of Initial Rate with BrO_3- ion Concentration

Beaker 1			Beaker2			Time (sec)
S.No.	$KBrO_3$ Solution (ml)	Water (ml)	KBr Solution (ml)	H_2SO_4 solution (B) (ml)	Phenol solution (A) (ml)	
1	10	0	10	15	1	t_1
2	8	2	10	15	1	t_2
3	6	4	10	15	1	t_3
4	5	5	10	15	1	t_4
5	4	6	10	15	1	t_5

The solutions are first brought to a constant temperature. For the experiment solution from beaker 1 is added into solution in beaker 2 and stop watch is started. The solution is poured rapidly between the two beakers and is set in the thermostat or over a white glazed tile. Note the timing when the colour of methyl orange completely disappears. The time will be found to be inversely proportional to the volume of $KBrO_3$solution used.

[III] Change of Initial Rate with H^+ ion Concentration

In this case, sulphuric acid is made without methyl orange and the concentration of KBr, $KBrO_3$ and other Reactants are increased to greater values than of H_2SO_4. Phenol solution used is the same solution (A). The new solution required are 0.01M H_2SO_4, 0.2 M $KBrO_3$ and 5×10^{-5} M phenol.

The solution (C) contain 12 g KBr and 5 ml of bench methyl orange solution in 250 ml of solution. This solution is nearly0.4 M in KBr. The following solution are now arranged in beakers .1 and 2

Beaker 1			Beaker2			Time (sec)
S.No.	H_2SO_4Solution (ml)	Water (ml)	$KBrO_3$Solution (ml)	KBr solution (C) (ml)	Phenol solution (A) (ml)	
1	10	0	10	15	1	t_1
2	8	2	10	15	1	t_2
3	6	4	10	15	1	t_3
4	5	5	10	15	1	t_4
5	4	6	10	15	1	t_5

In case the initial rate is very fast when 10 ml of H_2SO_4 solution is used, carry out the experiments further with lesser concentrated solution than before. In this case also the time increases as sulphuric acid concentration is decreases but they are not inversely proportional to the volume of H_2SO_4 used.

2.3.2.(d) Calculations:

The rate of reaction can be expressed in terms of formation of bromine. The rate equation can be written as

$$\frac{d[Br]}{dt} = k\,[Br^-]_t^x\,[BrO_3^-]_t^y[H^+]_t^z$$

The initial rate of reaction in each case is proportional to $[Br^-]_0^x\,[BrO_3^-]_0^y[H^+]_0^z$

As the two concentration have been taken as constant in each series of experiments, the initial rate can be taken as proportional to the concentration factor of the reactant which is changed. For change in H_2SO_4 Concentration $[H^+]_0$, we can express

$$\text{Initial rate, } r_1 \;\alpha\; [H^+]_0^z$$

$$\log r_t = z \log [H^+]_0 + \log c$$

A plot of log r_t against log $[H^+]_0$ should give a straight line with a slope equal to z. A non integral slope will suggest acomplex reaction kinetics and fractional order for reaction.

2.4 STUDY OF THE ADSORPTION OF AN ACID ON CHARCOAL AND TO PROVE THE VALIDITY OF FREUNDLICH ADSORPTION ISOTHERM.

2.4.1. Objective

To determine the adsorption of acetic acid on charcoal and prove the validity of Freundlich adsorption isotherm.

2.4.2. Requirements

Reagent bottles, burette, funnel, pipette, conical flask, whatman filter paper, 1M acetic acid, 0.25 M NaOH, Charcoal, Phenolphthalein indicator.

2.4.3. Theory

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and separate phase. Adsorbate means the material being adsorbed. Adsorbent means the solid material being used them as adsorbing phase.

Freundlich (1909) proposed an empirical equation to represent, in general, the adsorption relationship and is classically known as Freundlich adsorption isotherm. According to it,

$$x/m = K C^{1/n}$$

Where, x is the amount of solute adsorbed, m is the amount of adsorbing material, c is the equilibrium concentration of adsorbate in the solution, k is a constant depending upon the nature of both adsorbent and adsorbate, while n is another constant which is dependent on the nature of the adsorbate. The value of 1/n is generally less than unity. On taking logarithms of equation 1 we get,

$$\log x/m = \log k + 1/n \log C$$

if the values of log x/m are plotted as ordinate against log c as abscissa, we get a straight line, with slope, 1/n and intercept on the ordinate log k.

2.4.4. Procedure

Prepare N/ 2 acetic acid and N/10 NaOH by dilution method. Take six reagent bottles, clean and dry them. Now prepare the following solution in each bottle. Now place a stopper on each bottle and shake all the bottles thoroughly well, one after the other. The shaking should be done for at least one hour. Then allow them to stand. Filter each solution through a filter paper and collect the filtrate in numbered beakers. Reject the first 5 ml of each filtrate. Now pipette out 10 ml of each filtered solution in a conical flask and titrate it with N/10 NaOH solution, using phenolphthalein as an indicator. Repeat the titration with each solution till get two concordant readings for each solution.

Bottle	N/2 acetic acid (ml)	Distilled Water (ml)	Amount of Charcoal (g)
1	25	0	1.0
2	20	05	1.0
3	15	10	1.0
4	10	20	1.0
5	05	25	1.0

In the last and beginning, titrate the stock solution of acetic acid also by means of N/10 NaOH solution.

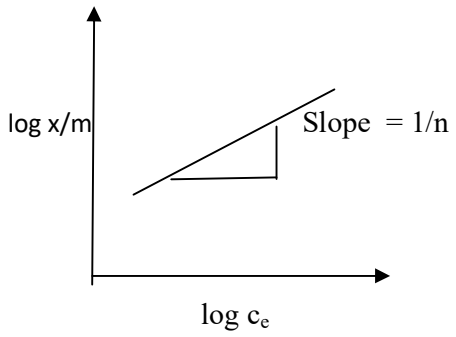
Observation: 10 ml of stock acetic acid solution = x l of N/10 NaOH

S. No.	Initial concentration (C_0) of acid before adsorption	Equilibrium Concentration (C_e) of acid after adsorption	Amount of acid (C_0 - C_e) adsorbed (ml of NaOH)
1	x	-	-
2	(4/5) x	-	-
3	(3/5) x	-	-
4	(1/2) x	-	-
5	(2/5) x	-	-

Calculations ;

$x = c_0 - c_e$ and m = 1 g each case

We can calculate x/m for each bottle and then find the value of log x/m. The logarithm of c_e terms is also noted in each case. Then the graph is plotted with log x/m as ordinate and log c_e as abscissa. we observe that it will be a straight line. The slope of this line will thus be equal to 1/n. This proves the validity of Freundlich adsorption isotherm.



2.4.5. Result

The validity of freundlich adsorption isotherm for the adsorption of acetic acid on charcoal had been tested.

'n' Value from graph = …….

'c' value from graph = ……

2.5. DETERMINATION OF PARTITION COEFFICIENTS.

2.5.1. Objective

To determine the partition coefficients of iodine between carbon tetra chloride and water.

2.5.2. Requirements

Reagent bottle, Burette, pipette, conical flask, Separating Funnel

2.5.3. Theory

Since Iodine exists in the same molecular state in both the solvents, the partition coefficient K will be given by

$$k = \frac{\text{Concentration of } I_2 \text{ in } CCl_4 \text{ layer}}{\text{concentration of } I_2 \text{ in } H_2O \text{ layer}}$$

2.5.4. Procedure

First of all prepare approximately 150 ml saturated solution of Iodine in carbon tetra chloride and filter. Now, take three reagent bottles and label them with numbers 1, 2 and 3. Now add the following things in them as specified as below:

Bottle 1:

40 ml saturated solution of iodine in CCl_4 + 0 ml of pure CCl_4 + 150 ml of distilled water.

Bottle 2:

30 ml saturated solution of iodine in CCl_4 + 10 ml pure CCl_4 + 150 ml of distilled water.

Bottle 3;

25 ml saturated solution of iodine in CCl_4 + 15 ml pure CCl_4 + 150 ml of distilled water.

Now place stopper on each bottle and shake for 20-30 minutes. The results of this experiment depend on how much the shaking is done. More the shaking, better are the results. Allow the mixture to separate into two layers. Now separate both carbon tetrachloride and water layers of each reagent bottle, by means of a separating funnel and place them into separate numbered bottles.

Now pipette 25 ml of the aqueous layer from bottle no 1 into a conical flask. Add 4-5 drops of starch solution. Now titrate against N/100 sodium thiosulphate solution. Repeat the process till

you get two concordant readings. Similarly, titrate 25 ml of each aqueous layer of the other two bottles numbered 2 and 3 against N/100 sodium thiosulphate solution.

Similarly, first take about 25 ml of water in a conical flask and pipette out 5 ml of the carbon tetra chloride layer of bottle no.1 into it and add about 4-5 drops of starch solution. The addition of water helps in the titration by gradually extracting iodine into water layer where the reaction with sodium thiosulphate occurs. By covering the carbon tetrachloride with water layer, loss of iodine vapour from the exposed solution is also prevented. Now the titrate it against H/10 sodium thiosulphate solution. Repeat the process till you get two concordant readings. Similarly, titrate 5 ml of the carbon tetra chloride layer of the other two bottles numbered 2 and 3 against N/10 sodium thio sulphate solution.

Observation:

Room temperature = t℃

	Titration with Aqueous Layer				**Titration With CCl_4 layer**			
Bottle No.	**Volume Taken (ml)**	**Initial Reading of burette (ml)**	**Final reading of burette (ml)**	**N/100 Hypo used (ml)**	**Volume Taken (ml)**	**Initial reading of burette (ml)**	**Final reading of burette (ml)**	**N/10 Hypo used (ml)**
1	25 25 25			V_2	5 5 5			V_3
2	25 25 25			V_2,	5 5 5			V_3,
3	25 25 25			V_2"	5 5 5			V_3"

Calculatios:

Bottle 1.

(a) For Water layer:

$N_1 \times 25 = N/100 \times V_2$

$N_1 = N \times V_2 / 25 \times 100$

Concentration (C_1) of I_2 in water layer

$= 127 \times V_2 / 25 \times 100$ g equivs/litre

(b) For CCl_4 layer

$N_1 \times 5 = N/10 \times V_3$

$N_1 = N \times V_3 / 5 \times 10$

Concentration (C_2) of I_2 in CCl_4 layer

$= 127 \times V_3 / 5 \times 10$ g equivs/litre

Partition coefficient, $K = C_2/C_1$

Similarly, we can find and calculate the partition coefficient of iodine between carbon tetrachloride and water for bottle no 2 and 3. We will see that for all the three bottles the values of K comes out to be nearly constant. Take the mean of all the three value.

2.5.5. Result

The partition coefficient of iodine between carbon tetra chloride and water is…….

2.6. DETERMINATION OF MOLECULAR SURFACE ENERGY AND ASSOCIATION FACTOR OF A LIQUID BY STALAGMOMETER OR DROP PIPETTE METHOD.

2.6.1. Objective

To determine the molecular surface energy and association factor of ethyl alcohol by stalagometer or drop pipette method.

2.6.2. Requirements

Stalagmometer, pyknometer, beaker etc.

2.6.3. Theory

If a liquid suspended in another liquid of the same density withwhich it neither mixes nor reacts, is withdrawn under the action of gravity., it assume a spherical shape. Molecular surface of the liquid is the surface of the sphere, taken up by one mole of liquid. It has been found that molecular surface are proportional to $V^{2/3}$, Where V is the molecular volume. The molecular surface energy of a liquid is then given by $\gamma V^{2/3}$, where γ = surface tension of the liquid. If v be the specific volume and M the molecular weight of the liquid then $V = \nu M$.

Therefore, molecular surface energy $= \gamma V^{2/3} = \gamma (M\nu)^{2/3}$

The molecular surface energy is a linear function of temperature and varies with temperature according to the relation

$$\gamma (M\nu)^{2/3} = K (T_c - t - 6)$$

Where, T_c and t are the critical temperature and observation temperature, respectively.

At two different temperature t_1 and t_2 we have

$$\gamma_1 (M\nu_1)^{2/3} = K (T_c - t_1 - 6)$$

$$\gamma_2 (M\nu_2)^{2/3} = K (T_c - t_2 - 6)$$

or

$$K = \frac{\gamma_1 (Mv_1)^{2/3} - \gamma_2 (Mv_2)^{2/3}}{t_2 - t_1}$$

$$K = \frac{\gamma_1 (M/d_1)^{2/3} - \gamma_2 (M/d_2)^{2/3}}{t_2 - t_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where, d_1 and d_2 are densities of the liquid at temperature t_1 and t_2 respectively.

Equqtion 1 is Known as Ramsay- Shield equation. The value of K for most of the non associated liquids is approximately equal to 2.12. But for associated liquids, the value of K is much lower than 2.12. if, however, the molecular weight is multiplied by a factor α, where α is greater than one , then a value of 2.12 is obtained for K. The factor α is known as association factor and gives the number of times the mean molecular weight of a liquid is greater than the normal molecular weight. Thus, for associated liquids, we have,

$$K = \frac{\gamma_1 \left(\alpha \frac{M}{d_1}\right)^{2/3} - \gamma_2 \left(\alpha \frac{M}{d_2}\right)^{2/3}}{t_2 - t_1} = 2.12 \quad \ldots\ldots\ldots\ldots \quad (2)$$

From equation 1 we have

$$K = \frac{\gamma_1 (M/d_1)^{2/3} - \gamma_2 (M/d_2)^{2/3}}{t_2 - t_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Therefore,dividing equation 2 by 3 we get,

$$\alpha = \left(\frac{2.12}{K}\right)^{3/2}$$

Thus the degree of association of a liquid may be calculated from above equation.

2.6.4. Procedure

The surface tension of ethyl alcohol determined at two different temperatures, say at room temperature and at 50℃ by stalagmometer method.

Thoroughly wash the stalagmometer first with chromic acid and then with distilled water. Rinse with alcohol and then dry. Attach a rubber tubing with pinch cock to the upper end of the stalagmometer. Clamp it in a vertical position and then suck distilled water until it reaches the mark in the apparatus. Regulate the flow of water with the help of the pinch cock such that 10 to 15 drop of water fall in per minute. The counting of drops starts as soon as the water meniscus passes the mark in a apparatus and stopped after it passes the lower mark in a apparatus. Repeat the process again at least 3-4 times.

Remove water from the stalagmometer, rinse it with alcohol and dry. Now fill the stalagmometer with ethyl alcohol up to mark in a apparatus. The number of drops are counted similarly as in the case of water. This process is also repeated 3-4 times. Then densities of ethyl alcohol are determined at the same two temperatures by means of a pyknometer or by density bottle.

Observations:

Weight of empty pyknometer = W_1 g

Weight of pyknometer + water = W_2g

Weight of Pyknometer + ethanol = W_3g

Liquid (Room Temperature)	Number of Drops	Surface tension
Water	**Mean value n_1**	γ_1
Ethanol	**Mean value n_2**	γ_2

Calculation:

$$\frac{\text{Density of liquid } (d_2)}{\text{Density of water } (d_1)} = \frac{\text{Weight of liquid}}{\text{weight of water}} = \frac{W_3}{W_2} = \frac{W_1}{W_1}$$

Surface tension of liquid $\gamma_1 = \gamma_2 \frac{n_2 d_1}{n_1 d_1}$

The molecular surface energy at both the temperatures can be calculated by the formula, $\gamma \left(\frac{M}{d_1}\right)^{2/3}$, as we know all the unknown factors.

Similarly, the value of K is calculated by means of equation.

$$K = \frac{\gamma_1 (M/d_1)^{2/3} - \gamma_2 (M/d_2)^{2/3}}{t_2 - t_1}$$

Once the value of K is Known, the value of association factor α, can be calculated by equation

$$\alpha = \left(\frac{2.12}{K}\right)^{3/2}$$

2.6.5. Result

The Molecular Surface energy = ……..

Association Factor = ……

2.7 TERMINAL QUESTIONS

Q.1. Define the adsorption.

Q.2.What do you mean by adsorption isotherm? Explain Freundlich adsorption isotherm for the adsorption of gases on solids.

Q.3. Define the distribution law with example.

Q.4. What is surface tension?

Q.4.What is the effect of temperature on surface tension?

Q.5. What is molar surface energy?

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BLOCK II: ORGANIC CHEMISTRY

UNIT 3: MULTI-STEP SYNTHESIS OF ORGANIC COMPOUNDS

Contents

3.1 INTRODUCTION

Organic Synthesis and procedure is of great importance in experimental chemistry. Topic includes preparative chemistry in association with synthesis, purification, yield and quality of products.

Various techniques are used in synthesis of organic compounds. Some important methods are listed below:

3.1.1 CLEANING THE APPARATUS

Since impurities especially tar and gummy matter can be easily removed in fresh condition, it is advantageous to clean laboratory glassware immediately after use. First we should wash the glass apparatus with water. It removes gummy material easily. Water insoluble impurities can be removed by washing them with soapy solution and sometimes with hot water. Some impurities can also be removed by using organic solvents. For this purpose acetone, petroleum ether, benzene can be used.

3.1.2 DRYING THE APPARATUS

The apparatus can be dried by standing it over night. Beaker, flasks, test tubes etc. should be inverted in such a way as to drainage water easily. For immediate drying, the apparatus may be rinsed with a bit of acetone and allowed to dry. For this purpose, highly volatile other solvents like methanol or ethanol can be used in place of acetone but these evaporate less quickly.

3.1.3 DRYING AGENTS

In the preparation of organic compounds, it is sometimes necessary to dry the reagents. Due to the water in the reagent, the following problems may arise:

i) The presence of water may bring about an undesired hydrolytic reaction.

ii) It may exert and adverse catalytic effect in the reaction.

iii) It may slow down or even inhibit completely the desired reaction.

To dry an organic solid, spread its thin film and place it in the exposure of the air at room temperature. In his way, we cannot remove completely the entire water so either heat it in a drying oven at temperature below its melting or decomposition point, or put it in a desiccator

containing some drying agents. Some drying agents are: anhydrous calcium chloride ($CaCl_2$), potassium pentaoxide (P_2O_5), quick lime (CaO), sodium sulphate (Na_2SO_4) etc.

An organic liquid is generally dried by placing it in direct contact with solid drying agents in a closed vessel. Some common drying agents are anhydrous inorganic salts. The organic liquid is shaken thoroughly with drying agents in a closed bottle. Allow it to stand overnight. The dried liquid is now filtered to remove the drying agent and may be distilled (*if necessary*).A good drying agent should have the following characteristics:

- It should be cheap.
- It must remove the water.
- It must not react with the solvent or dissolve in it.
- The ability to absorb water should be great.
- It is easy to use.

Some common drying agents for organic compounds

Hydrocarbons	Anhydrous Calcium Chloride ,Anhydrous Calcium Sulphate, Metallic sulphate Sodium , Phosphorous Pentaoxide
Alocohols	Anhydrous Potassium carbonate , Anhydrous Potassium Sulphate,Quick lime
Amines	Solid Sodium hydroxide , Solid Potassium hydroxide, Quick lime
Organic Acids	Anhydrous Magnesium sulphate, Sodium Sulphate, Calcium Sulphate
Alkyl halides / Aryl halides	Anhydrous Calcium Chloride, Anhydrous Calcium Sulphate, Phosphorous Pentaoxide.
Aldehydes	Anhydrous Magnesium sulphate, Calcium Sulphate, Sodium sulphate
Ketones	Anhydrous Potassium Carbonate, Anhydrous Potassium sulphate

Note: *Phosphorous pentaoxide is difficult to handle as it causes serve burns on the skin.*

Sodium metal should be handled with the tongs.

3.1.4. MAINTENANCE OF THE REACTION MIXTURE

A definite temperature is also maintained sometimes to prepare an organic compound. Some methods have to be adopted to keep the temperature above the room temperature, depending upon the temperature requirement. For example, water bath can be used if 100^{o}C temperatures is required. Brine bath can be used for temperature 105-106 ^{o}C. In this method, a little sodium chloride if added to water. By doing so, the boiling point of water increases from 5-6 ^{o}C. Temperature above 100 ^{o}C and up to 200 ^{o}C, requires oil bath. For very high temperatures, sand bath may be used. On the other hand, if temperature below room temperature is required, then ice bath is used.

3.1.5 REFLUXING

In order to prepare an organic compound, it is necessary sometimes to heat the reaction mixture for a long period of time at an approximately constant temperature. The simplest procedure is refluxing.

Reflux is a technique involving the condensation to the system from it originates. The way to reflux depends on the nature of solvent used. The two different ways of refluxing are:

i)Refluxing using water condenser: In this method, the solvent used has low boiling points e.g. benzene. The apparatus used is shown in fig.31.

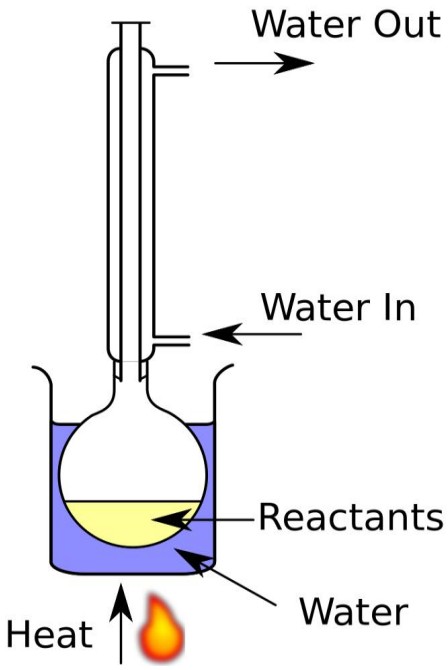


Fig. 3.1: Apparatus of Refluxing using water condenser

ii) Refluxing using air condenser: In this method, the solvent used has higher boiling point such as water. The air condenser used is shown in fig. 3.2.

iii) Heating may be done via wire gauge or a suitable bath (Water, oil, sand etc.) depending upon the reaction mixture to reflux.

Fig 3.2: Air condenser

3.1.6 DISTILLATION

This is the most important method to separate the volatile components and also to purify the organic liquids. Distillation involves two steps:

i) Vaporization: In this process, liquid is converted into vapours.

ii) Condensation: In this process, vapours again converted into liquids.

Several distillation methods are used but the type of distillation depends mainly on the nature of impurities present in the organic liquids. The important distillation methods are: simple distillation, fractional distillation, vacuum distillation, steam distillation etc.

3.1.6.1 SIMPLE DISTILLATION

Simple distillation is applied only for liquids which boil without decomposition at atmospheric pressure and contains either non volatile impurities or liquids with large differences in their boiling points. The necessary apparatus used in simple distillation are distillation flask, thermometer, Leibig condenser and receiver. The apparatus is set as shown in fig. 3.3.

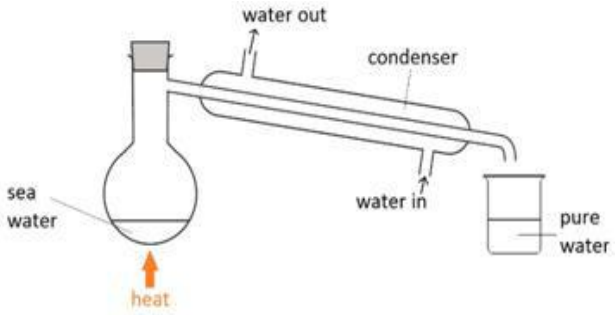


Fig.3.3: Apparatus of simple distillation

The impure liquid is taken in distillation flask up to half of the capacity of the flask which is connected to thermometer and Leibig's condenser.

The flask is heated on wire gauze (if liquid is non inflammable) or a water bath, oil bath or sand bath (depends on the boiling point of the liquid). The liquid boils and converts into vapours, then passes through condenser and condenses. The pure liquid is collected in the receiver while the non volatile impurities are left behind.

Precautions: i) To avoid bumping, a few pieces of broken porcelain dish should be added to the distillation flask.

ii) The water pump must be connected with the apparatus through a safety flask provided with a stop cock to prevent water from drawn back into the distilling system or the manometer.

iii) The lower end of thermometer should be just below the position where the side tube is fused and should not be dipped into the solution.

iv) While changing receivers remove the flame beneath the bath, and allow the distilling flask to cool slightly before releasing vacuum. After changing the receiver, the system should first be evacuated again before heating is continued.

Example: Nitrobenzene synthesized in the laboratory can be purified by this method.

3.1.6.2 FRACTIONAL DISTILLATION

When the liquids present in the mixture have their boiling points close to each other, the separation is difficult. The fractions are always contaminated. The fractions are further purified by repeated distillations. To decrease the numbers of distillations, the separation is done by fitting the distillation flask with fractionating column. In this method, fractionating column is used which allows partition one liquid to be distilled over at one temperature and then different liquids may be collected at different temperature range. One of the various fractionating columns is given in the fig. 3.4.

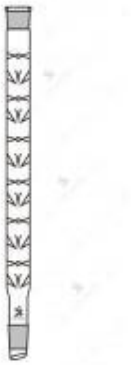


Fig 3.4: Fractionating column

Example: A mixture of methanol and propanol or a mixture of benzene and toluene may be separated by this technique.

The fractionating distillation assembly set is shown in the fig 3.5.

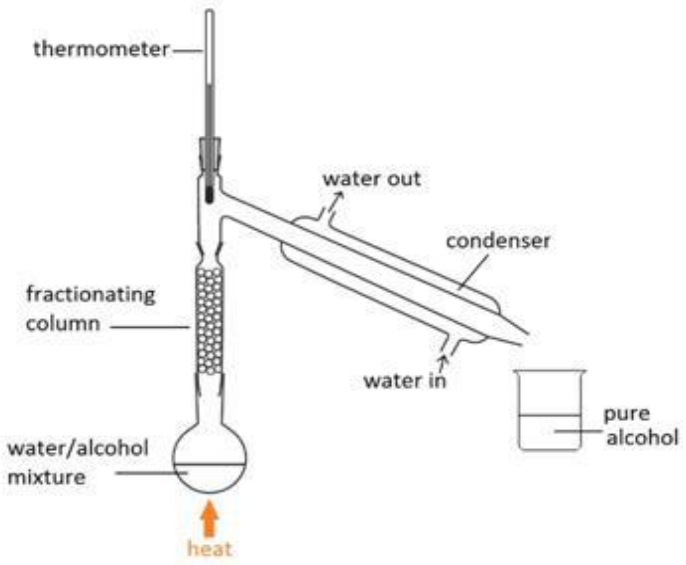


Fig.3.5: Apparatus for fractional distillation

3.1.6.3 VACUUM DISTILLATION

Some organic compounds undergo partial or complete decomposition before their boiling point hence these cannot be distilled under atmospheric pressure. For example: glycerine is one such compound which decomposes at its boiling point. A special apparatus shown in fig. 6. is used for this purpose. It consists of a Claisen's flask which has two necks. In one of the neck a thermometer is fitted while in the other a capillary tube whose lower end is dipped in the liquid and upper end is closed by means of rubber tubing and a screw clip through which a very slow current of air is admitted. This device is prevented the bumping. A filtration flask, which is used as a receiver is connected to a suction pump through a manometer. Fig. 3.6

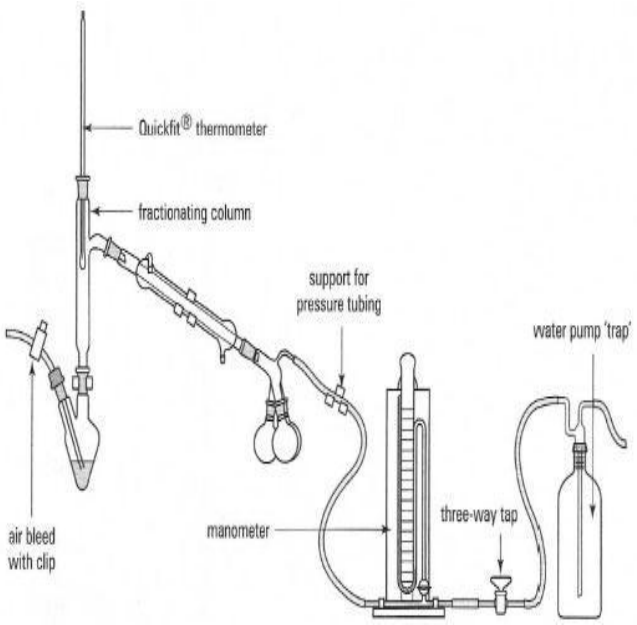


Fig.3.6: Apparatus for vacuum distillation

Vacuum distillation is not only useful in avoiding decomposition but also serve to economise fuel for industrial concerns.

3.1.6.4 STEAM DISTILLATION

The liquids which are soluble in steam and contain non volatile impurities are purified by steam distillation method. In this method, the substance is placed in a round bottom flask which is heated in order to boil. The vapours of pure substance with the steam passes through condenser leaving behinds the impurities and collect in the receiver. The condensate is a mixture of organic substance and water. The two being immiscible are separated with the help of a separating funnel. The apparatus employed in steam distillation is shown inthe Fig37.

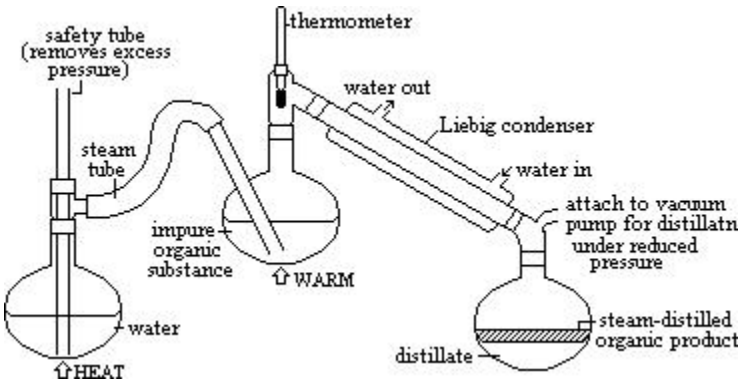


Fig.3.7: Apparatus for steam distillation

Example: This process is used in the purification of compounds such as chloro toluenes, aniline and nitrobenzene. It is also employed in the isolation of essential oils from flowers.

3.1.6.5 EXTRACTION WITH SOLVENTS

The process of separation of organic compounds from its aqueous solution by shaking with a suitable organic solvent is termed solvent extraction. The solvent should be immiscible in water and the organic compounds to be separated should be highly soluble in it.

The aqueous solution is taken in a separating funnel. A small quantity of the solvent is added to it. It will form a separate layer as being immiscible with water. The mouth of the funnel is closed and the contents are shaken. The organic substance being more soluble in the solvent is transferred from aqueous layer to solvent layer. The separating funnel is kept stationary for some times during which two distinct layers are formed. The lower layer is taken out by opening the tap of the funnel. The organic substance is recovered from solvent layer by distillation. It is considered better always to extract 3 or 4 times with smaller amounts of the solvent rather than once the bulk of the solvent.Fig 3.8

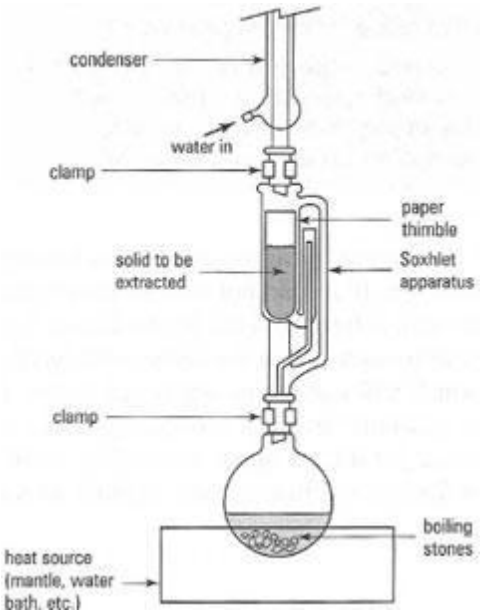


Fig 3.8: Apparatus for solvent extraction

3.1.7 DECOLOURIZATION

Sometimes, it is possible to adsorb an undesired coloured compound by heating a solution with an adsorbent such as activated charcoal or alumina and then filtering the mixture to remove the adsorbent and the adsorbed material.

Occasionally, it may be possible to decolourize a solution by filtering it through a short column of alumina. This preferentially adsorb the coloured substance. A poorly adsorbed solvent like ether, benzene, n-hexane etc. must be used so that the solvent will not take the place of the coloured material.

3.1.8 RECRYSTALLIZATION

It involves the preparation of solution of impure compound in a suitable solvent at a higher temperature i.e. near its boiling point. The solution so formed is filtered. The filtrate is kept

undisturbed for some times. The cooling occurs and the crystals of the pure compound separate out. In case the compounds separates out as an oil, the filtrate is reheated until a clear solution results, and then it is cooled spontaneously with constant stirring and scratching the wall of the container with glass rod.

3.1.9 WASHING

The residue on the filter paper of the funnel must always be washed, in order to remove mother liquor, generally with the solvent used for recrystallization and then with water (in case water insoluble residue).

3.1.10 DRYING

The solid is dries on the pads of the filter papers. It is then kept in a desiccator or in oven depending on the melting point on the compounds as to make it completely dry.

3.1.11 CHROMATOGRAPHY

It is recent and most efficient techniques which were first introduced by Tswatt for the separation of coloured substances into individual components. Chromatography is based on the selective distribution of the various constituents of a mixture between two phases, a stationary and a mobile phase. Different constituents migrate at different rates through the stationary phases. The stationary phase can be solid or liquid while the moving phase can be a liquid or a gas. Based on the nature of the stationary phase and the moving phase, different types of chromatographic techniques have been developed. The most common are:

i) *Column chromatography*

ii) *Paper chromatography*

iii) *Thin layer chromatography*

iv) *Gas chromatography*

v) *Ion exchange chromatography*

3.1.12 CRITERIA OF PURITY OF ORGANIC COMPOUNDS

After purification the test of purity of organic compounds is the next important step. A pure organic compound possesses characteristic physical properties such as specific rotation, boiling point, melting point, crystalline structure etc. if a purified sample shows the same properties that the pure substance is known to possess, it may be considered as pure and no further purification is required.

It is noted that a pure organic compound solid or liquid has a definite and sharp melting or boiling point while an impure substance has a lower or higher and indefinite melting or boiling point.

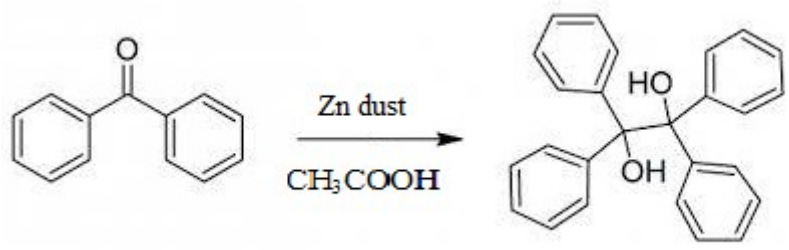
3.2 EXPERIMENT No.1: PREPARATION OF BENZOPINACOLONE

3.2.1 OBJECT: PREPARATION OF BENZOPINACOLONE FROM BENZOPHENONE AS FOLLOW

Benzophenone ⟶ Benzopinacol ⟶ Benzopinacolone

3.2.1.1 STEP I: PREPARATION OF BENZOPINACOL FROM BENZOPHENONE

3.2.1.1a REACTION



Benzophenone **Benzopinacol**

3.2.1.1b REAGENTS

Benzophenone	5.0g
Zinc dust	2.5g
Glacial Acetic Acid	75ml
Water	15ml

3.2.1.1c PROCEDURE

Take 5.0 g of benzophenone, 2.5 g of zinc dust, and 75 ml of glacial acetic acid and 15 ml of water in a flask fitted with reflux water condenser. Heat the reaction mixture for 2 hours. Now cool and then filter to obtain benzopinacol precipitate. Crystallize it from glacial acetic acid.

Yield	3.0g
Melting Point	188°c
Appearance	Colourless Crystalline Solid

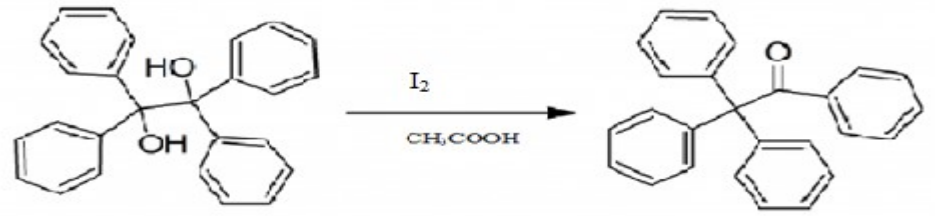
3.2.1.2 STEP II: PREPARATION OF BENZOPINACOLONE FROM BENZOPINACOL

3.2.1.2a NAME OF REACTION

Pinacol-Pinacolone rearrangement

Benzophenone first converted into benzopinacol with zinc dust and acetic acid. Benzopinacol so formed is dehydrated by boiling with an acid to form benzopinacolone. The conversion of benzapinacol to benzapinacolone is an example of pinacol-pinacolone rearrangement.

3.2.1.2b REACTION



Benzopinacol Benzopinacolone

3.2.1.2c REAGENTS

Benzopinacol	2.0g
Glacial acetic acid	20ml
Iodine	0.05g

3.2.1.2d PROCEDURE

Take 2.0 g of benzopinacol (prepared in step I), 0.05 g of iodine and 20 ml of glacial acetic acid in a flask fitted with the reflux water condenser. Heat the reaction mixture for 20 minutes. Cool the contents and then filter. Wash the residue with ethanol to remove iodine.

Yield	1.6 g
Melting point	178◦C
Appearance	Colourless crystalline solid

3.2.1.2e PRECAUTION

Benzopicacolone should be washed thoroughly with ethanol to remove iodine completely.

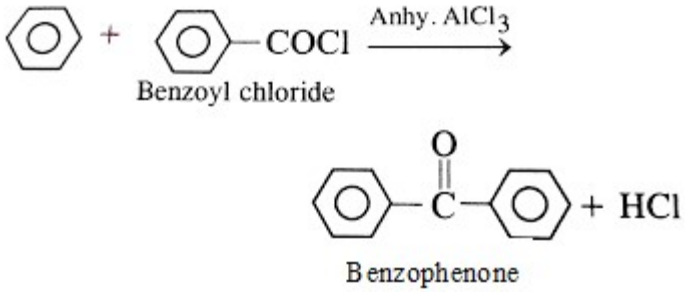
3.3 EXPERIMENT No. 2 PREPARATION OF BENZANILIDE

3.3.1 OBJECT: PREPARATION OF BENZANILIDE FROM BENZENE AS FOLLOW

Benzene → benzophenone → benzophenone oxime → benzanilide

3.3.1.1 STEP 1: PREPARATION OF BENZOPHENONE FROM BENZENE

3.1.1.1a REACTION



3.1.1.1.b REAGENTS

Benzoyl chloride	4.8 g (or 3.9 ml)
Dry Benzene	20 ml
Anhydrous $AlCl_3$	3 5 g
Concentrated HCl	17 ml
5% NaOH Solution	
Anhydrous $MgSO_4$	

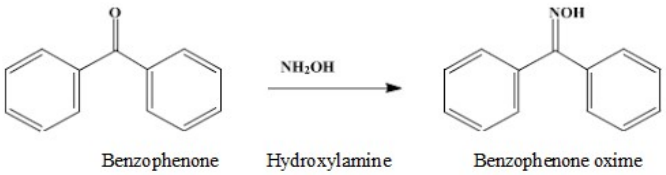
3.1.1.1.c PROCEDURE

In a 100 ml round bottom flask, place 4.8 g (or 3.9ml) of benzoyl chloride and 20 ml of dry benzene and to it add 5 g of finely powered anhydrous aluminium chloride slowly- slowly and with frequent shaking. Reflux the contents on a water bath for 3 hours and then pour the warm contents to a mixture of 50 grams of ice and 17 ml of concentrated HCl. Filter (if necessary) it, separate the upper benzene layer, wash it with water. Dry the products with anhydrous $MgSO_4$ remove the benzene with the help of air bath. Now cool the reaction mixture and then distilled under reduced pressure. Collect the product at 187-190^{o}C/ 15 mm. pressure the product solidifies soon on cooling.

Yield	5.0 g
Melting Point	47-48°C
Appearance	White solid

3.3.1.2 STEP 2: PREPARATION OF BENZOPHENONE OXIME FROM BENZOPHENONE

3.1.1.2.a REACTION



3.1.1.2.b REAGENTS

Benzophenone	3.0 g
Hydroxylamine hydrochloride	2.0 g
Rectified spirit	10 ml
Sodium hydroxide pellet	3.5 g
Conc. Hydrochloric Acid	10 ml
Methanol for recrystalization	

3.1.1.2.c PROCEDURE

In a round bottom flask take 3.0 g of benzophenone, 2.0 g of hydroxylamine hydrochloride, and 10 ml of rectified spirit. Now add 3.5 g sodium hydroxide pellet in portions with shaking. If the reaction becomes vigorous, cool it under tap water. Now boil the contents with a reflux condenser for 5 minutes. Cool it and pour the content into a solution of 10 ml concentrated hydrochloric acid in 75 ml of water taken in a 500 ml beaker. Filter the precipitate, wash it thoroughly with water and dry it in desiccators. Recrystallize the product from methyl alcohol.

Yield	3.0 g
Melting	142 °C
Appearance	Crystalline Solid

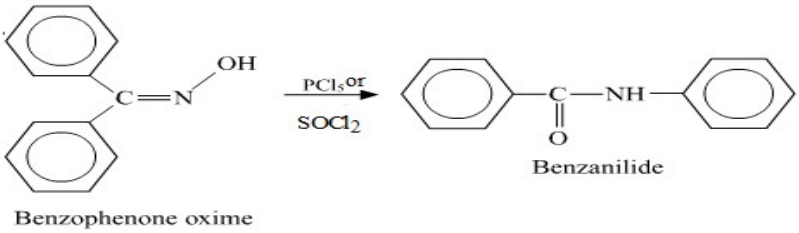
3.1.1.2.d PRECAUTION

As the benzophenone oxime is gradually decomposed by oxygen and moisture in benzophenone

and nitric acid, it should, therefore, be preserved in vacuum desiccators

3.3.1.3STEP3:PREPARATION OF BENZANILIDE FROM BENZOPHENONE OXIME

3.1.1.3.a REACTION



Benzophenone oxime Benzanilide

3.1.1.3.b REAGENTS

Benzophenone oxine	3.0g
Phosphorous pentachloride	5.0g
or	
Thionyl chloride	5 ml
Anhydrous ether	30ml

3.1.1.3.c PROCEDURE

In a conical flask, dissolve 3.0 g of benzophenone oxime in 30 ml of anhydrous ether by shaking on a water bath carefully. Now add 5.0g of phosphorous penta chloride or 5 ml of thionyl chloride. Shake the contents and distill off the ether on a water bath carefully. Now add 30 ml of water and then boil for approximately 15 minutes. Decent the supernatant liquid and recrystallize the benzanilide formed in the same vessel from boiling ethanol.

Yield	2.5 g
Melting point	163°C
Appearance:	White crystalline solid

3.4. EXPERIMENT No. 3 PREPARATION OF BENZILIC ACID

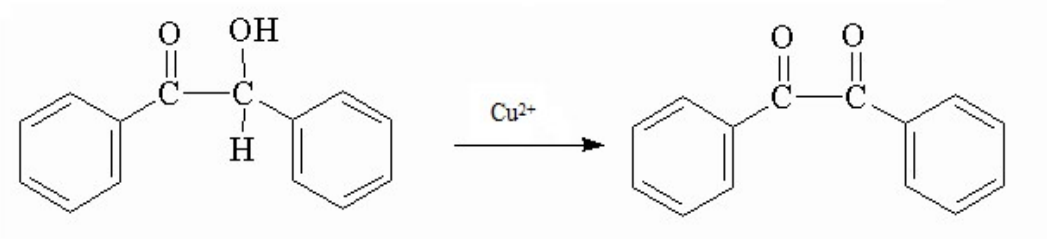
3.4.1 OBJECT: PREPARATION OF BENZILIC ACID FROM BENZOIN AS FOLLOW

Benzoin ⟶ benzyl ⟶ Benzilic acid

3.4.1.1 STEP 1: PREPARATION OF BENZIL FROM BENZOIN BY MEANS OF CUPRIC SALT

I Method (Oxidation)

Reaction:



Benzoin Benzil

3.4.1.1a REAGENTS

Benzoin	5.0 g
Glacial acetic acid	15 ml
Ammonium nitrate	2.5 g
Cupric acetate solution (2%)	3.0 ml
Ice	

3.4.1.1b PROCEDURE

In a 250 ml round bottom flask, place 5.0 g of benzoin, 15 ml of glacial acetic acid, and 2.5 g of pulverized ammonium nitrate and 3 ml of a 2 % cupric acetate solution. *(A 2% cupric acetate solution is prepared by dissolving 2.0 g of cupric acetate monohydrate in 80ml of 10% aqueous acetic acid, stirring well and then filtering the solution to remove basic copper salt that is precipitated)*. Add a bit boiling chips and then reflux the solution first gently on a wire gauze with occasional swirling when the evaluation of nitrogen commences and then strongly for one and half hours, cool the solution to 50-60^{o}C and pour it into 40 ml of ice water with stirring. After sometimes, filter the crystals on suction. Wash them thoroughly with water and dry by pressing on a filter paper. The product may be purified by recrystallization from methyl alcohol or 75% aqueous ethanol.

Yield 4-5 g

Melting Point 95◦C

Appearance Yellow Crystals

II Method

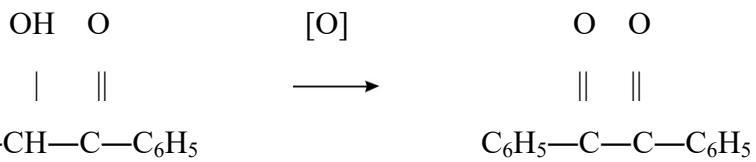
3.4.1.2 PREPARATION OF BENZIL FROM BENZOIN BY MEANS OF NITRIC ACID

(Oxidation)

3.4.1.2a REACTION

i) $2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$

ii)



Benzoin **Benzil**

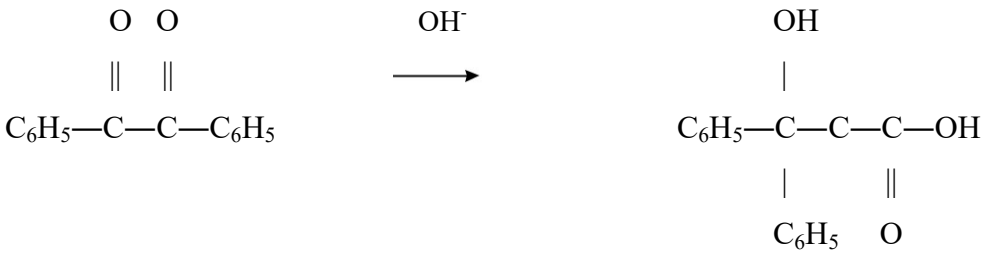
3.4.1.2.b REAGENTS

Benzoin	5.0g
Glacial Acetic Acid	25 ml
Concentrated HNO_3	12.5 g
Ice	

In a 250 ml round bottom flask place 5.0 g of benzoin, 25 ml of glacial acetic acid and 12.5 ml of conc. Nitric acid. Swirl the flask vigorously and then heat the reaction mixture on a steam bath for 2 hours. Cool the flask in an ice bath, add 100 ml of water, mix thoroughly and allow the yellow precipitate of benzil to settle. The product may be purified by recrystallization from methanol or 75 % aqueous ethanol.

Yield	4-5 g
Melting Point	95 ◦C
Appearance	Yellow crystals

3.4.1.3 STEP 2: PREPARATION OF BENZILIC ACID FROM BENZIL *(Benzilic acid rearrangement)*



Benzil **Benzilic Acid**

3.4.1.3.b REAGENTS

Benzil	5.0 g

KOH	5.0 g
Ethanol	15 ml
HCl(1M)	15 ml

3.4.1.3.c PROCEDURE

In a 100 ml round bottom flask dissolve 5.0 g of KOH in 10 ml water and add 15 ml of ethanol and 5.0 g of benzil to it. Reflux the mixture on water bath for 20-30 minutes. Transfer the contents of the flask in to the porcelain dish and keep overnight at room temperature. Collect crystals of potassium salt of benzilic acid by suction filteration and wash with ice cold water. Now dissolve potassium benzilate in 20 ml water and then add drop wise with stirring concentrated HCl until the solution is acidic and then cool. Benzilic acid will precipitate as a red brown sticky mass. Filter the precipitated product through Buchner funnel and wash with cold water. Dissolved the coloured sticky mass in minimum amount of water, add a pinch of decolourizing carbon to it, heat on water bath for few seconds and filter hot. Cool the filtrate and collect crystals of benzilic acid.

Yield	2.0 g
Melting point	148-150°C
Appearance	White solid

3.5 SYNTHESIS OF HETEROCYCLIC COMPOUNDS

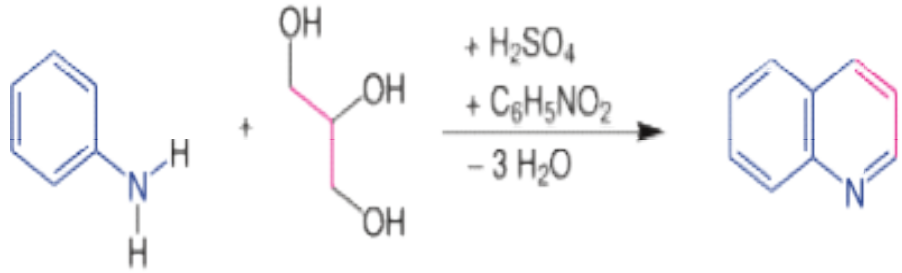
3.5.1 EXPERIMENT No. 4 PREPARATION OF QUINOLINE

3.5.1.1 OBJECT: PREPARATION OF QUINOLINE FROM ANILINE

3.5.1.1a SKRAUP SYNTHESIS

The Skraup synthesis is a chemical reaction used to synthesize quinolines. In the Skraup reaction, aniline is heated with sulfuric acid, glycerol, and an oxidizing agent such as nitrobenzene to yield quinoline. In this reaction, nitrobenzene serves as both the solvent and the oxidizing agent. The reaction, which otherwise has a reputation for being violent, is typically conducted in the presence of ferrous sulphate.

3.5.1.1b REACTION



Aniline Glycerol Quinoline

3.5.1.1c REAGENTS

Aniline	38.0 g
Crystaline $FeSO_4$	15.0 g
Glycerol	120.0 g
Nitrobenzene	24.0g
Conc. Sulphuric Acid	100g
$NaNO_2$	8.0-10.0 g
Hydrochloric Acid	
Sodium Hydroxide	
Ether	

24.0 g nitrobenzene, 38.0 g aniline, 120.0 g glycerine, and 100.0 g concentrated sulfuric acid are cautiously mixed in a flask of 1-liter capacity, and heated together under reflux condenser, until the reaction just begins. If the flame is removed this does not proceed too vigorously. When it is finished the liquid is kept boiling for two hours longer, then it is

diluted with water and the nitrobenzene distilled off in steam. The solution is rendered alkaline with sodium hydroxide and again distilled with steam. The distillate contains quinoline and aniline. To remove aniline the mixture is treated with an excess of hydrochloric acid, and sodium nitrite is then added until the smell of nitrous acid persists even on shaking, the solution is heated to boiling until all the diazobenzene is destroyed (i.e. till the evolution of gas has ceased). The liquid now made alkaline again with caustic soda and distilled with steam. The distillate is extracted with ether, the ether is evaporated and the residual quinoline dried with solid caustic potash and distilled.

Yield 40.0 g

Boiling Point 237°C

Appearance Yellowish oily liquid

*(*if the reaction proceeds too violently at the beginning, the reflux condenser may be assisted by placing a wet towel over the upper part of the flask*)

3.5.1.1e PRECAUTIONS

1) The reaction is always violent.

2)In general, glycerol contains an appreciable amount of water so the product yield is much lower.

3) The material should be added in correct order.

4) It is therefore necessary that the steam passing through the condenser should be sufficiently rapid to cause it to form a uniform film over the receiving flask.

3.5.2 EXPERIMENT No. 5: PREPARATION OF 2-PHENYL INDOLE

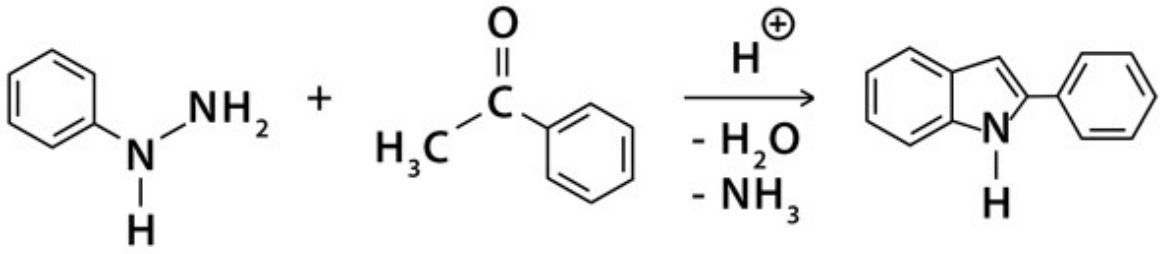
3.5.2.1 OBJECT: PREPARATION OF 2-PHENYL INDOLE FROM PHENYLHYDRAZINE

3.5.2.1.a *Fischer Indole Synthesis*

Fischer Indole synthesis involves the reaction between the phenylhydrazone of an aldehyde or ketone and an acid catalyst such as zinc chloride, ethanolic hydrogen chloride or acetic acid. Cyclization (in the formation of indole derivative) occurs during the course of reaction with the loss of ammonia molecule.

3.5.2.1.b REACTION

Fischer Indole Synthesis



Phenylhydrazine Acetophenone 2-Phenylindole

3.5.2.1.1 STEP I: SYNTHESIS OF PHENYLHYDRAZONE FROM PHENYLHYDRAZINE

3.5.2.1.1.a REAGENTS

Acetophenole	5 ml
Glacial acetic acid	25 ml
Phenylhydrazine	6 ml

3.5.2.1.1.b PROCEDURE

Method I

In a 100 ml conical flask, dissolve 5 ml of acetophenone in 15 ml of glacial acetic acid. In another 100 ml conical flask, dissolve 6 ml of phenylhydrazine in a mixture of 10 ml of glacial acetic acid and 10 ml of water. Now add hydrazine solution to that of acetophenone solution and shake the solution vigorously for 10-15 minutes. The mixture (heat it for 10-15 min if required becomes warm and phenylhydrazone separates out. Recrystallize the phenylhydrazone from ethanol.

Yield 5.0 -6.0 g

Melting point 105 °C

Appearance Solid

Method II

In a 50 ml round bottom flask fitted with reflux condenser, heat the mixture of 5 ml of acetophenone with 6 ml of phenylhydrazine on a water bath for 1 hour. Cool the flask and stir

with glass rod until the mixture solidifies. Filter the crystalline acetophenone phenylhydrazone. Recrystallize it from ethanol.

Yield 5.0-5.5 g

Melting point 105 °C

Appearance Solid

**Caution! Hydrazines are toxic and should be handled in a hood. Anhydrous hydrazine is extremely reactive with oxidizing agents (including air) and should always be used behind a protective screen.*

3.5.2.1.2 STEP II: SYNTHESIS OF 2-PHENYL INDOLE FROM PHENYLHYDRAZONE

3.5.2.1.2.a REAGENTS

Phenyl hydrazone 5.0g

Polyphosphoric acid 30.0 g

Ethanol 50 ml

3.5.2.1.2.b PROCEDURE

In a 100 ml round bottom flask, take 5.0 g of phenylhydrazone and 30.0 g of polyphosphoric acid. Heat the flask on water bath with stirring for 10-15 minutes. Cool, and then add 50 ml of cold water to the flask and stir. Filter the precipitated solid at pump and wash with water. Reflux the crude product with 50 ml of ethanol, add a little animal charcoal and filter the solution while still hot through a pre-heated metallic funnel. Cool the filtrate and collect crystals of 2-Phenyl indole.

Yield 3.0-3.5 g

Melting point 188-189 °C

Appearance solid

3.6 *SOME ENZYMATIC REACTIONS*

3.6.1 EXPERIMENT NO. 6 CONVERSION OF A LOW SWEET GLUCOSE TO A HIGH SWEET FRUCTOSE

3.6.1.1 OBJECT: TO SHOW HOW ENZYMES DERIVED FROM MICROORGANISMS CAN BE USED TO CONVERT SUGARS, i.e. FROM A LOW SWEET GLUCOSE TO A HIGH SWEET FRUCTOSE.

3.6.1.1a REAGENTS:

Glucose/Dextrose Solution (8%)

Glucose Isomerase

Magnesium Sulfate or Magnesium Chloride (5 mg)

3.6.1.1. b PROCEDURE

Before starting the experiment, test the glucose solution for level of sweetness by using glucose test strips to measure the glucose content. In a 250 mL beaker, place 100 mL of the glucose solution. Now add magnesium salt into it. Then add 1.0 g of the enzyme. Place the beaker into a water bath at temperature 60 °C with occasionally stirring. After 20 min., test for level of remaining glucose using test strips; repeat every 20 min for 1 hour and test the level of sweetness in the final solution.

3.6.2 EXPERIMENT NO. 7 CONVERSION OF STARCH TO SUGAR

3.6.2.1 OBJECT: TO CONVERT STARCH TO SUGAR (CHEMICAL DETERMINATION)

3.6.2.1a MATERIAL

Potato starch 1.0 g

Iodine solution 1 drop

3.6.2.1.b PROCEDURE

Place 1.0 g of potato starch in a labeled test tube containing 16 ml of water, mix well and then place the tube in a water bath at temperature 37ºC. In a second labeled test tube, mix 1 g of potato starch, 15 ml of water, and 1 ml of saliva and then place in a water bath at same temperature 37ºC. Incubate the tubes for 15 minutes, then remove from the water bath and add 1 drop of iodine solution to each test tube. It should be observed that starch will bind iodine and thus acquire a blue-black color. However, in the tube that contains the saliva, the amylase in the saliva will have hydrolyzed the starch into sugar, which is unable to bind iodine.

Note: This experiment requires the tasting of products therefore human grade materials and uncontaminated equipment need to be used.

3.6.3 EXPERIMENT No.8 DENATURING THE PROTEIN FOUND IN EGG WHITE

3.6.3.1 OBJECT: TO PERFORM THE EXPERIMENT WITH DIFFERENT METHODS OF DENATURING THE PROTEIN FOUND IN EGG WHITE (ALBUMIN)

3.6.3.1.a MATERIALS

6 raw eggs

NaCl

$NaHCO_3$

Lemon juice

1% Ag NO_3 (Heavy metals are not allowed in food supply)

3.6.3.1.b BACKGROUND

Proteins are large molecules made up of small amino acids. Proteins are held in a natural shape due to the interaction of side groups on the amino acids from one part of the molecule to another area of the molecule. These interactions may be hydrogen bonds or disulfide bonds. We can denature the proteins by disrupting the H-bonds that are within the structure.

When this happens the overall shape of the protein changes and new properties can be observed. The shape of a protein is associated with food processing properties, such as solubility, gel formation, and enzyme activity. In the egg whites the albumin will change from clear to white.

We will explore how the following denature egg albumin.

i) Heat – done by cooking

ii) Acids & bases – can form ions on some side groups of amino acids

iii) Organic compounds – form their own hydrogen bonds with the amino acids

iv) Heavy metals – react with disulfide bonds

3.6.3.1.c PROCEDURE

In a 400 mL beaker, place 300 mL of water, place on ring stand and heat to boiling. Take six test tubes and label them with numbers 1-6. Separate 3 eggs, placing the egg white in a test tube until half filled. Discard the egg yolk. Place test tube labeled with no. 1 in the boiling water and allows to "cook" till egg turns white. Add NaCl to test tube labeled with no. 2 and stir. Add $NaHCO_3$ to test tube labeled with no. 3 and stir. Add lemon juice to test tube labeled with no. 4 and stir. Add rectified alcohol to test tube labeled with no. 5 and stir. Add 1% $AgNO_3$ to test tube labeled with no. 6.

Record observations on the table below:

3.6.3.1.d DATA TABLE

Test Tube	Added	Observations
1	Heat	
2	NaCl – Ionic Compound	

3	$NaHCO_3$ –Base	
4	Lemon juice –Acid	
5	Rectified alcohol organic liquid	
6	$AgNO_3$ – heavy Metal	

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9. All diagrams are taken from Wikipedia, Google Search and Tutomyself, 1:07 Describe Experimental Techniques for the separation of mixtures Including Simple distillation. Fractional distillation, Crystallization and paper chromatography (last accessed date 20 January 2018).

10. All structures are made with the help of Chem Draw Software.

BLOCK II: ORGANIC CHEMISTRY

UNIT 4: ENZYMATIC REDUCTION

4.1 Introduction

4.2 Objective

4.3 Reduction of ethyl acetoacetate using baker's yeast to yield enantiomeric excess of S (+) ethyl-3-hydroxybutanoate and determine its optical purity.

4.4 Bio synthesis of ethanol from sucrose.

4.5 Synthesis using microwaves: Benzylation of diethyl malonate with benzyl chloride.

4.6 Synthesis using phase transfer catalyst: Alkylation of diethyl malonate or ethylacetoacetate. with an alkyl halide.

4.7 Terminal questions

4.8 References

4.1 INTRODUCTION

In recent years, chemists have devised a number of chiral reducing agents, but few of them are as efficient as the enzymatic reducing agents found in nature. One experiment will introduce you to the methods of using a benign organism—Baker's yeast—to carry out a synthetic organic transformation. Enzymes, which are protein catalysts, can also be isolated from organisms such as yeast and used directly to carry out a desired reaction. The use of whole organism or individual enzyme is desirable as the chemical reactions happen at ambient temperature and pressure, but they also usually require large amount of water that must be properly disposed as waste.

Pasteur in 1857 described fermentation as the action of a living organism. Edward Buchner made a cell free extract of yeast that caused the conversion of sugar (sucrose) to alcohol observing that the extract contained catalysts. In 1905 Harden discovered that inorganic phosphate increased the rate of fermentation and was consumed.

A baker makes use of fermentation by taking advantage of the gas released to leaven the bread. Baker's yeast is used to convert sucrose, table sugar, into ethanol and carbon dioxide with the aid of 14 enzymes as catalysts present in yeast. Sucrose (table sugar) is a disaccharide that is split into two simple sugars glucose and fructose by enzymes. Thirty one kilocalories of heat is released per mole of glucose consumed in the sequence of anaerobic (no oxygen present) reactions. Fructose is converted to ethanol in the same way as glucose. Glucose is converted via a number of reactions involving enzymes to form pyruvic acid. A decarboxylase converts pyruvic acid to acetaldehyde in fermentation. Yeast alcohol dehydrogenase, a highly studied enzyme, catalyzes the reduction of acetaldehyde to ethanol. The fermentation reaction must be protected from exposure to oxygen because under aerobic conditions acetobacteria can convert ethanol to acetic acid (vinegar). So the fermentation reaction must occur in the absence of oxygen (anaerobic) to prevent the conversion of sugar into vinegar.

Microwaves, as the name implies are very short waves. However, microwave really indicates the wavelengths in the micron region. Microwave frequencies are up to infrared and visible light region and refer to those from 1GHz to 106 GHz. Most domestic and commercial microwave

ovens operate at 2.45 GHz. There are two primary mechanisms for the absorption of microwave energy by a solution.

(i) Dipole rotation
(ii) Ionic conductance

In the dipole rotation mechanism, molecular dipole is aligned with the applied electric field. The electric field oscillates, forcing the dipole molecules to move and the resulting friction heats the solution. At 2.45 GHz, the frequency of most laboratory microwave oven, the dipole align and randomize five billion times a second. The frequency of the molecular rotation is similar to the frequency of microwave radiation and consequently the molecule continuously attempts to realign itself with the changing field and the energy is absorbed. In the ionic conduction mechanism, the ion species migrate in one direction or the other according to the polarity of the electromagnetic field. Heating is the natural consequence when the accelerated ions meet resistance to their flow.

Microwave (MW) radiation exposure can significantly speed up reactions and increase the exit of the targeted materials, reducing the resorption in organic synthesis. MW radiation is a crucial tool for the development of green chemistry. Advantages of this method are - lack of heat, cleanliness of the reaction, practical instantaneous heating of the reaction mass to the given temperature and, in particular, replacing the traditional solvent with an elevated and polar solvent. It is known, that the combination of the MW–PTC techniques was used in the alkylation of active methylene containing substrates such as diethyl malonate.

4.2 OBJECTIVE

Students will learn following particularly from this unit:

- Understanding of microbial growth processes, fermentation processes and chemistry.
- Calculation of the optical purity and enzymatic reduction of carbonyl compound.
- Synthesis of alkylation and benzylation of diethymalonate using Microwave and Phase Transfer Catalyst.

4.3 REDUCTION OF ETHYL ACETOACETATE USING BAKER'S YEAST TO YIELD ENANTIOMERIC EXCESS OF S (+) ETHYL-3-HYDROXYBUTANOATE AND DETERMINE ITS OPTICAL PURITY.

4.3.1(a). Object

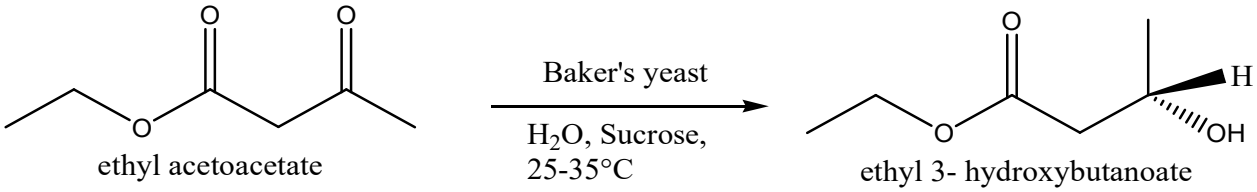
To study the chiral reduction of ethyl acetoacetate using baker's yeast.

4.3.2. Requirements

Erlenmeyer flask, rubber stopper, solution of barium hydroxide, magnetic stirring bar.

4.3.3. Theory

In this experiment we use common baker's yeast as a chiral reducing agent to transform an achiral starting material, ethyl acetoacetate into chiral product, (S) (+) ethyl-3-hydroxybutanoate. The chiral product is used as an important building block in the laboratory synthesis of natural products. The product ethyl-3- hydroxybutanoate is formed principally as the enatiomer with (S)(+) configuration. The reaction does produce a small amount of opposite enantiomer (R)- (-)-ethyl-3-hydroxybutanoate.



ethyl acetoacetate — ethyl 3- hydroxybutanoate

4.3.4. Procedure

In First week

Take a 250 ml Erlenmeyer flask and dissolve 40.0 g of sucrose, 0.25 g of di sodium hydrogen phosphate (Na_2HPO_4) in 150 ml of warm (35℃) tap water. After that add approximately 8.0 g of baker's yeast and swirl to suspend the yeast throughout the solution. In about 15 minutes, add 1.5 g of ethyl acetoacetate. Put some cotton in the mouth of the flask stopper (but still allow gas to escape) label the flask and store the flask in the oven at 25-35 °C until the next week.

In Second Week

Add approx 5.0 g of celite filtration aid to the flask and remove the yeast cells by filtration with Buchner Funnel. Wash the cells with water and gently scrape the filter paper to remove excess yeast cells. Saturate the filtrate with sodium chloride to reduce solubility of the product. Extract the saline solution 5× 25 ml portion of diethyl ether. Shaking too vigorously may lead to the formation of an emulsion at the interface, which can be broken up with a small amount of methanol. Dry the ether layer over anhydrous sodium sulphate. After 5-10 minutes of drying gravity filter and the ether solution into pre-weighed 250 ml round bottom flask. Remove the ether, using the rotary evaporator.

4.3.5. Result

- Record the actual yield…….
- Obtain ^{1}HNMR and IR spectrum……
- A chiral GC of the sample…..

4.3.1. (b) Object

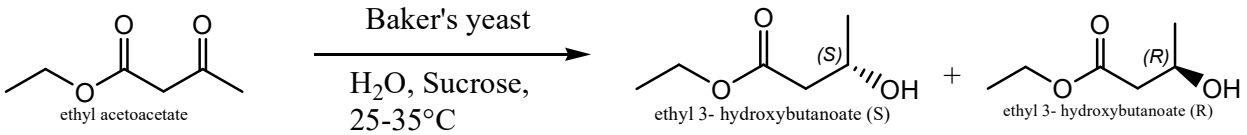
To determine the optical purity of enantiomeric excess of S (+) ethyl-3-hydroxybentanoate obtained from reduction of ethyl acetoacetate by baker's yeast.

4.3.2. Requirements

NMR spectrometer

4.3.3. Theory

The reduction of ethyl acetoacetate produce a product that is predominantly the (S)-(+) enantiomer of 3-hydroxybutanoate. In this procedure, use NMR to determine the actual purity of the product. In the NMR spectrum there is no visible difference between the two enantiomers. In the NMR spectrum methyl hydrogen (both side terminal CH_3) appear at about 1.25 ppm, methylene hydrogen appear at about 2.4 ppm and hydroxyl proton appears at 3.6 ppm. Rest two methylene (nearer to oxygen atom) and methine proton (nearer to hydroxyl group) appear at about 4.2 ppm.



There is a method that will allow the spectra of the two enatiomers to be distinguished. This method is to use a chiral shift reagent. These reagent "spread out" the resonance of the compound with which they are used, increasing the chemical shift of proton that are nearest the centre of the metal complex by the largest amount. The two enantiomers which are chiral will interact differently with the chiral shift reagent. The complex formed from the (R) and (S) isomers with (+)- camphor containing shift reagent will be diastereomer. Diastereomer usually have different physical properties and the NMR spectra are no exception. The two complexes will be formed with slightly differing geometries. Although the effect is small, it is large enough to begin to see difference in the NMR spectra of the two enantiomer. In particular, the originally superimposed methylene and methine multiplets will be resolved.

The Chiral Shift Reagent used in this experiment is tris[3- (heptafloropropyl-hydroxymethylene)-(+)-camphorato}europium (II) or Eu (hfc). In this complex, the europium is in chiral environment because it is complexed to camphor which is chiral molecule.

4.3.4. Procedure

Using a Pasteur pipette to aid the transfer, weigh 0.035 g of chiral ethyl 3--hydroxybutanoate from above experiment directly into an NMR tube. Weigh 8–11mg of *tris*[3-(heptafluoropropylhydroxymethylene)-(1)-camphorato]europium(III)chiral shift reagent on a piece of weighing paper and add the chiral shift reagent to the chiral hydroxyl ester in the NMR tube. Take care to avoid chipping the fragile NMR tube while adding the shift reagent with a micro spatula. Add $CDCl_3$ solvent to the NMR tube until the level reaches 50 mm. Cap the tube and invert it to mix the sample. Allow the NMR sample to stand for a minimum of about 5–8 minutes before determining the NMR spectrum. Record in your notebook the exact weights of sample and chiral shift reagent that you have used. Record the NMR spectrum of the sample.

Alternate Procedure for optical purity:

The optical purity of the product can be determined by measuring the optical rotation in a polarimeter. The specific rotation, $[\alpha]_D^{25^\circ C}$ of S(+)-ethyl-3-hydroxybutanoate has been reported to vary from +31.30 to 41.70° in methanol. The specific rotation, $[\alpha]_D^{25^\circ C}$, of 37.20° corresponds to an enantiomeric excess of 85%.

4.3.5. Result:

The peaks of interest are the methyl protons, doublet and triplet. Note that the doublet and triplet peaks for the two methyl groups in the racemic ethyl 3-hydroxybutanoate are doubled. The downfield doublet (1.412 and 1.391 ppm) and triplet (1.322, 1.298, and 1.274 ppm) peaks are assigned to the (*S*)-enantiomer. The upfield doublet (1.405 and 1.384 ppm) and triplet (1.316, 1.293, and 1.269 ppm) peaks are assigned to the (*R*)-enantiomer. The (*R*)-enantiomer in the triplet pattern by integration, determine the percentages of the (*S*)- and (*R*)-enantiomers in the chiral ethyl 3-hydroxybutanoate from above experiment. We should still find that the doublet and triplet for the (*S*)-enantiomer will always be downfield relative to the (*R*)-enantiomer.The assignments for the (*S*)- and (*R*)-enantiomers determined by obtaining the NMR spectrum of pure samples of each enantiomer in the presence of the chiral shift reagent. We may have noticed that the doublet has moved further downfield relative to the triplet.The reason for this is that the complexation of the chiral shift reagent occurs at the hydroxyl group. Because the methyl group is closer to the europium atom, it is expected that, this group will be shifted further downfield relative to the other methyl group.

4.4. BIO SYNTHESIS OF ETHANOL FROM SUCROSE.

4.4.1. Object

To separate ethanol from a fermentation mixture by distillation

4.4.2. Requirements

Erlenmeyer flask, glucose, bent glass tube, fractional distillation apparatus, round bottom flask, volumetric pipette etc.

4.4.3. Theory

Either sucrose or maltose can be used as the starting material for making ethanol. Sucrose is a disaccharide with the formula $C_{12}H_{22}O_{11}$. It has one glucose molecule combined with fructose. Maltose consists of two glucose molecules. The enzyme invertase is used to catalyze the hydrolysis of sucrose. Maltase is more effective in catalyzing the hydrolysis of maltose. Zymase is used to convert the hydrolyzed sugars to alcohol and carbon dioxide. Pasteur observed that

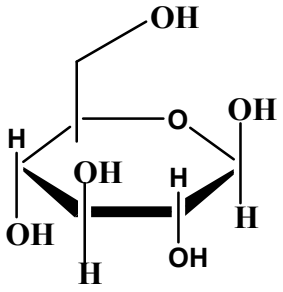
growth and fermentation were promoted by adding small amounts of mineral salts to the nutrient medium.

Later, it was found that before fermentation actually begins, the hexose sugars combine with phosphoric acid, and the resulting hexose–phosphoric acid combination is then degraded into carbon dioxide and ethanol. The carbon dioxide is not wasted in the commercial process, because it is converted to dry ice.

Energy: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$

Growth (anaerobic or aerobic): $C_6H_{12}O_6 (+ O_2) \rightarrow \text{biomass}$

Secondary metabolites: $C_6H_{12}O_6 \rightarrow 2 \text{ ethanol} + 2CO_2$



Yeast

$2\ CH_3CH_2OH + 2CO_2$

D-glucose **ethanol**

The fermentation is inhibited by its end product ethanol. It is not possible to prepare solutions containing more than 10–15% ethanol by this method. More concentrated ethanol can be isolated by fractional distillation. Ethanol and water form an azeotropic mixture consisting of 95% ethanol and 5% water by weight, which is the most concentrated ethanol that can be obtained by fractionation of dilute ethanol– water mixtures.

4.4.4. Procedure

Fermentation:

Take a 250 ml Erlenmeyer flask and then add to it about 20.0 g of glucose then add 75 ml of warm (not hot) water and swirl to dissolve. Add about 1.0-2.0 g of yeast stir gently until everything is well mixed. Stopper the flask with a one-hole rubber stopper containing a bent glass tube. Store this reaction in your drawer for 1-2 weeks while the fermentation reaction occurs.

Distillation:

Assemble a simple or fractional distillation apparatus with boiling stones, decanting the glucose/ ethanol solution into the 250 ml round bottom flask (RBF). Avoid transferring the yeast residue.

Distill the ethanol slowly collecting 5 ml fractions at periodic intervals. Record the temperature range for each fraction collected. Stop the collection at 97 °C. Determine the density of each fraction by measuring in a capped vial or stoppered test tube with a sample of known volume collected with a volumetric pipette. Determine the alcohol content of each fraction by:

1) Calculating density

2)Combine the ethanol fractions that are:

i) 50-80% concentration in one tube & record total volume.

ii) 80-96% concentration in another tube & record the volume

3)Calculate the % recovery from the amount of glucose used.

4) Test the flammability of your ethanol by igniting a few drops of your product on a watch glass.

Analysis of Distillate

Determine the total weight of the distillate. Determine the approximate density of distillate by transferring a known volume of the liquid with an automatic pipette or graduated pipette to a tared vial. Reweigh the vial and calculate the density. This method is good to two significant figures. Using the following table, determine the percentage composition by weight of ethanol in your distillate from the density of your sample. The extent of purification of the ethanol is limited because ethanol and water form a constant-boiling mixture, an azeotrope, with a composition of 95% ethanol and 5% water.

Density g/ 20ml	**% by weight**	**% by vol. (ml)**	**g /100 ml**
0.989	5	6.27	4.95
0.982	10	12.44	9.82
0.975	15	18.54	14.63
0.969	20	24.54	19.37
0.962	25	30.46	24.04
0.954	30	36.25	28.61
0.945	35	41.90	33.07
0.935	40	47.40	37.41
0.925	45	52.72	41.61
0.914	50	57.89	45.69

0.903	55	62.89	49.64
0.891	60	67.74	53.47
0.880	65	72.43	57.17

Example: Using the above chart a sample that has a density of 0.914 g/ml would have a composition of 50 % by weight (50 g EtOH/100 g solution) or 57.89 % by volume (57.89 mlEtOH/100 ml solution) or 45.69 g EtOH/100 ml solution.

4.4.5. Result

Yield of alcohol; ……..

4.5 SYNTHESIS USING MICROWAVE: BENZYLATION OF DIETHYL MALONATE WITH BENZYL CHLORIDE.

4.5.1. Object

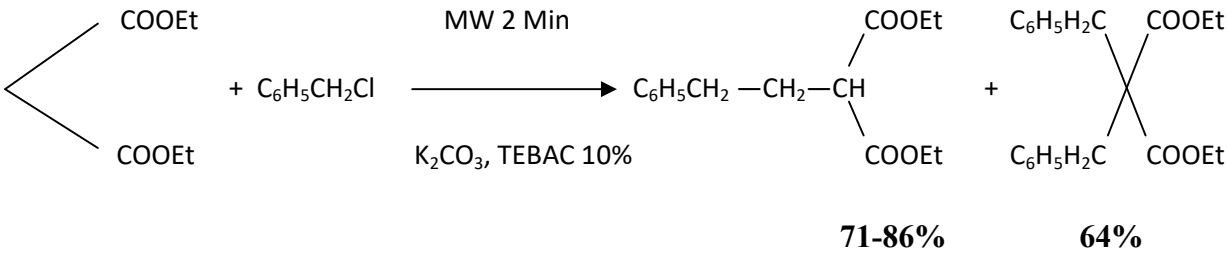
To synthesize diethyl benzyl malonate from diethyl malonate and benzyl chloride by using microwave.

4.5.2. Requirements

Flask**,** Diethyl malonate, Benzyl chloride, Sodium sulphate, Microwave oven, diethyl ether, aqueous solution of KOH etc.

4.5.3. Theory

Alkylation of the title compounds is a well-known and well-studied reaction. However, the use of the MW technique is relatively new in this area. The alkylating agents were different alkyl halides, such as normal and substituted benzyl chloride, allyl bromide and butyl bromide. K_2CO_3 (4 equiv.) was applied as the base, and 10% of TEBAC (triethylbenzylammonium chloride) was used as the phase transfer catalyst. The *C*-alkylated derivatives of acetoacetic ester were obtained in a 59%–82% yield. The benzylation of diethyl malonate with the more reactive benzyl bromide resulted in a yield of 68% after a 45 min irradiation at 180 °C. The use of a phase transfer catalyst led to the formation of by-products. The two by-products, $BnCH_2CO_2Et$ and $(Bn)_2CHCO_2Et$ may have been formed by the de-ethoxycarbonylation of diethyl benzylmalonate and diethyl dibenzylmalonate, respectively.



Benzylation of diethylmalonate under microwave condition

4.5.4. Procedure : There are two procedure for benzylation of diethyl malonate**.**

i) Benzylation in PTC "liquid-liquid" system with MW radiation

A flask with a mixture of 13.0g (0.1mol) of diethyl malonate, 15.18g (0.12mol) of benzyl chloride, 2.28g (0.01mol) of, 20ml 10N (0.2mol) aqueous solution of KOH was placed in a MW oven. The process continued for 10minutes. The reaction mixture was extracted with diethyl ether, the ether extract was dried over sodium sulphate, and the ether was distilled from the ether solution. The reaction products were investigated by liquid chromatography. The reaction process was characterized on the basis of the amount of ethyl alcohol detected.

ii) Benzylation in PTC "solid-liquid" system with MW radiation

A flask with a mixture of 16.0g (0.1mol) of diethyl malonate, 15.18g (0.12mol) of Benzyl chloride, 2.28g (0.01mol) of TEBAC (triethylbenzylammonium chloride), 11.2g (0.2mol) of dry powder of KOH was placed in a MW oven. The process continues for 10minutes.The reaction mixture was extracted with diethyl ether, the ether extract was dried over sodium sulphate, and excess ether was distilled from the ether solution. The reaction products were examined by liquid chromatography.

4.5.5. Result

IR and GC-Ms data.

4.6 *SYNTHESIS USING PHASE TRANSFER CATALYST: ALKYLATION OF DIETHYL MALONATE OR ETHYLACETOACETATE WITH AN ALKYL HALIDE.*

4.6.1. Object

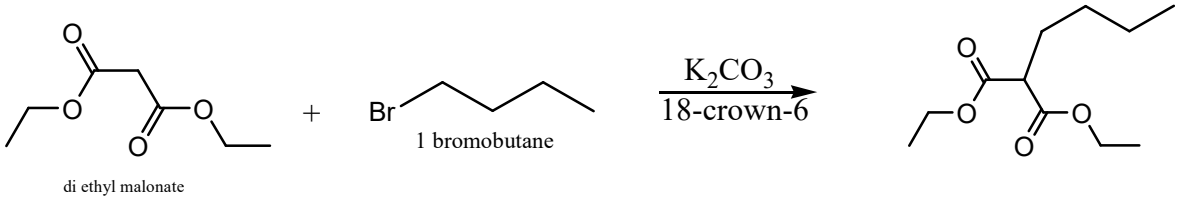
To investigate the alkylation of diethyl malonate by alkyl halide using phase transfer catalyst.

4.6.2. Requirements

Long-necked round-bottom flask, Erlenmeyer flask , anhydrous potassium carbonate, 1-bromobutane, diethyl malonate, 18-crown-6 phase, dichloromethane, pipette, NaCl etc.

4.6.3. Theory

Active methylene compounds contain two electron withdrawing groups, such as carbonyl groups, adjacent to a C-H bond, making the hydrogen relatively acidic. A liquid solid two phase system using *anhydrous* K_2CO_3 or Na_2CO_3 has the added advantage of absorbing the water formed in the reaction, thus minimizing ester hydrolysis. Since diethylmalonate has two acidic α (alpha) hydrogens, it can be dialkylated(a minor product of this reaction) by reaction with two equivalents of an alkyl halide. In this experiment solid K_2CO_3 is used as the base and the cyclic polyether, 18-crown-6, is used as the phase transfer catalyst to prepare 2-(n-butyl)-diethyl malonate from diethyl malonate and 1-bromobutane.



Alkylation of diethyl malonate by phase transfer catalyst

4.6.4. Procedure

0.4 g of anhydrous potassium carbonate put in 5-ml long-necked round-bottom flask and add one by one 0.30 ml of 1- bromobutane (0.38 g, 2.8 mmol), 0.38 ml of diethyl malonate (0.40 g, 2.5 mmol), 0.25 ml of 18-crown-6 phase transfer catalyst solution (5% in acetonitrile). After that add

a 1/2-inch magnetic stir bar and cap the flask with a rubber septum and needle. Gently heat the mixture on the *top* of a shallow sand bath for 2 hr with constant vigorous stirring.

Remove the 1/2-inch stir bar, add 1 ml of dichloromethane and 2 ml of distilled water. Mix vigorously with pipette to effect extraction into the organic layer. Remove the dichloromethane layer with a pipette, placing it into a reaction tube, and repeat the extraction with another 1 ml of dichloromethane, combining the organic layers. Wash the dichloromethane extracts with 2 ml standard aqueous NaCl, and dry over anhydrous Na_2SO_4, add the drying agent until it no longer clumps together and then let the solution stand for about 10 minutes. Remove the dichloromethane to a clean, dry, pre-weighed 10-ml Erlenmeyer flask and let the bulk of the dichloromethane evaporate. In the next lab period, remove the last traces of dichloromethane until a constant product weight is obtained by aspirating the flask in a bell jar. The product is a viscous yellow liquid (yield is approx. 400 mg). Check product purity and identity by gas chromatography, followed by GC-MS if your GC results are equivocal.

4.6.5. Result;

Analyse the data of GC-MS**.**

4.7 Terminal questions

Q.1. Draw the structures of: ethyl acetoacetate, (L)-tartaric acid, (R)-ethyl-3- hydroxybutyrate, and (S)-ethyl 3-hydroxybutanoate.

Q.2. Using yeast, can glucose be converted to ethanol? Can fructose be converted to ethanol?

Q.3. What are enantiomers? Why they are optically active?

Q.4. What is the biological reducing agent that gives rise to the formation of chiral ethyl 3-hydroxybutanoate?

Q.5. What are enzymes?

Q.6. What is an azeotropic mixture?

Q.7. Write a balanced equation for the conversion of sucrose into ethanol.

Q.8. Use resonance structures to explain why diethylmalonate may be easily deprotonated.

4.8 References

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1) N. Pohl, A.Clague, and K. Schwarz, (2002), Chiral Compounds and Green Chemistry:Reduction of a ketone by sodium borohydride and baker's yeast, J.Chem.Ed., 79, 6, 727.

2) Donald L. Pavia, Gary M, Lampman, George S. Kriz and Randall G. Engel, (2011).A Microscale Approach to Organic Laboratory Techniques, 5th edition, brooks/cole laboratory series for organic chemistry.

3) G. H.Torosyan and N. R.Hovhannisyan, (2018).Benzylation of 1,3-diketons in the phase transfer catalysis condition by microwave irradiation, *MOJ Biorg Org Chem.*;2, 217–219. Williamson, K.L.; Minard, R.; Masters, K.M., (2011).Macroscale and Microscale Organic Experiments, 6th Ed. Houghton Mifflin Co.: Boston, , 774.

4) D.Thompson and P.Reeves,(1985)."Phase-transfer-catalyzed Alkylation of Ethyl Acetoacetateand Diethyl Malonate", J. Chem. Ed., 6 2, , 907-908.)

BLOCK II: ORGANIC CHEMISTRY

UNIT 5: PAPER CHROMATOGRAPHY/THIN LAYER CHROMATOGRAPHY

Contents:

UNIT 5.1: OBJECTIVES

The objectives of this unit are to make aware the readers about separation technique basically chromatyography like thin layer chromatography, paper chromatography etc. The other aim of this unit is separation and identification of the sugars present in the given mixture of glucose, fructose and sucrose etc. using paper and thin layer chromatography and determination of R_f value.

UNIT 5.2: INTRODUCTION

The term chromatography wae coined by M. Tswett a Russian botanist in the year 1901 during his research on plant pigments. M. Tswett used the technique to separate various plant pigments such as chlorophylls, xanthophylls and carotenoids. Because of the appearance of colored band during the separation of pigment he named the technique chromatography (chrom = colour, graphy. = writing) because of it's mimically resemblance with with colour writing. The technique is also used for the separation of colorless mixtures in todays science hence is also known as separation technique. Based on the above facts chromatography is defined as "***The separation technique used for separation, purification, quantification, identification, analysis etc. due to differential migration of the components in a mixture between two immiscible phases, the stationary and mobile phase***." Based on interactions of solute with stationary and moblile phase involved in chromatography is adsorption and partition type. Paper chromatography is partition type while thin layer chromatography is adsorption type. Paper chromatography can be developed by:

Ascending mode. Fig 5.1

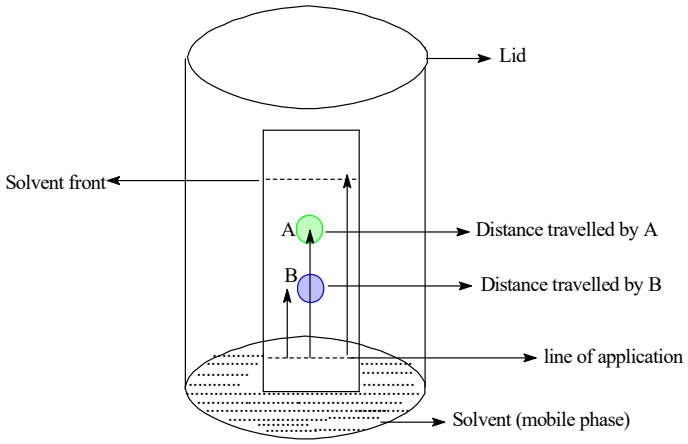
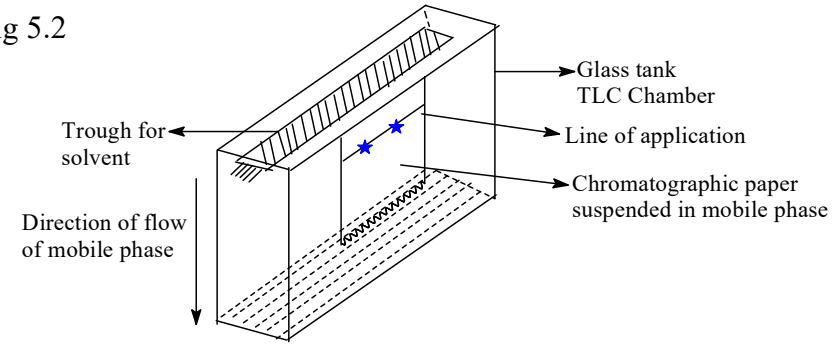


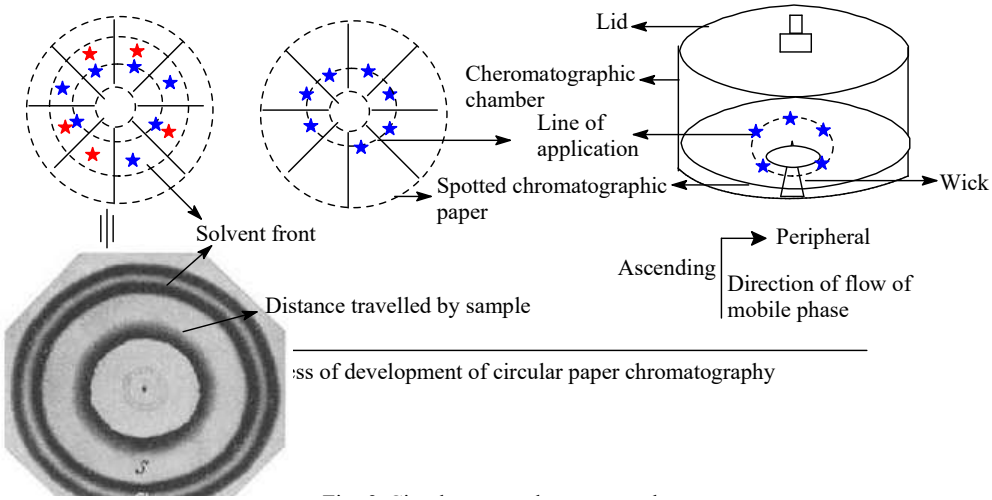
Fig 5.1 Ascending paper chromatography

Descending mode. Fig 5.2



Descending paper chromatography

Circular mode. Fig 5 3



Circular paper chromatography

The analysis/ identification of components in paper chromatography is done by matching the R_f (retardation factor. i.e the force that drag back the components towards line of application aginst propelling force due to capillary action) values of component separated with R_f of standard components co-spoted. The R_f is calculated as follow Fig 5.4.

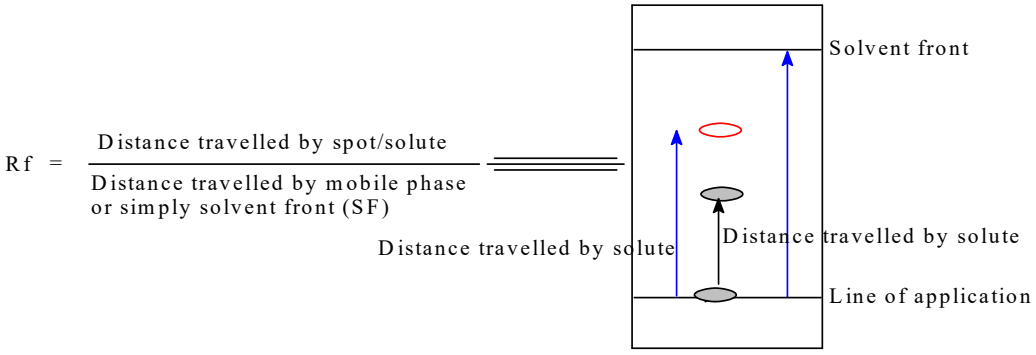


Fig 5.4 Measurment of R_f value

UNIT 5.3: THIN LAYER CHROMATOGRAPHY (TLC)

TLC is performed by spreading a stationary phase on inert supporting material like glass plates. Aluminium foil, polymeric material etc. Based on thickness coated on supporting material the TLC can be developed as analytical or preparative mode. Thin-layer chromatography can be used to monitor the progress of a reaction, identify compounds present in a given mixture, and determine the purity of a substance. The different steps involved in TLC are selection of inert support, saturation of TLC chamber, preparation of TLC plates by spreading uniformly the slurry of stationary phase either manually or by using spreader, drying of TLC plates, activation in oven, partial deactivation, spotting, development, air drying after demarking solvent front, visualization and calculation of R_f value as shown in Fig 5.4. The entire process for performing TLC has been illustrated in Fig.5.5. For quantitative analysis preparative TLC is performed. In preparative TLC concentrated continuous spotting is done and after development the different bands are scratched by spatula and dissolved in solvents. The solvent is stirred and filtered to get the components in filtrate. The entire process can be performed as shown in Fig 5.6

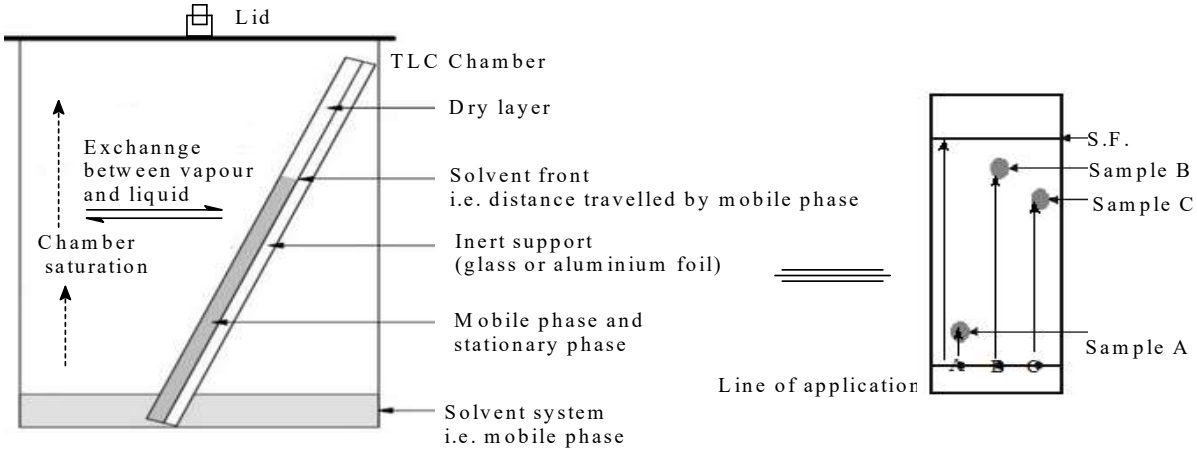


Fig 5.5 Processes of performing thin layer chromatography

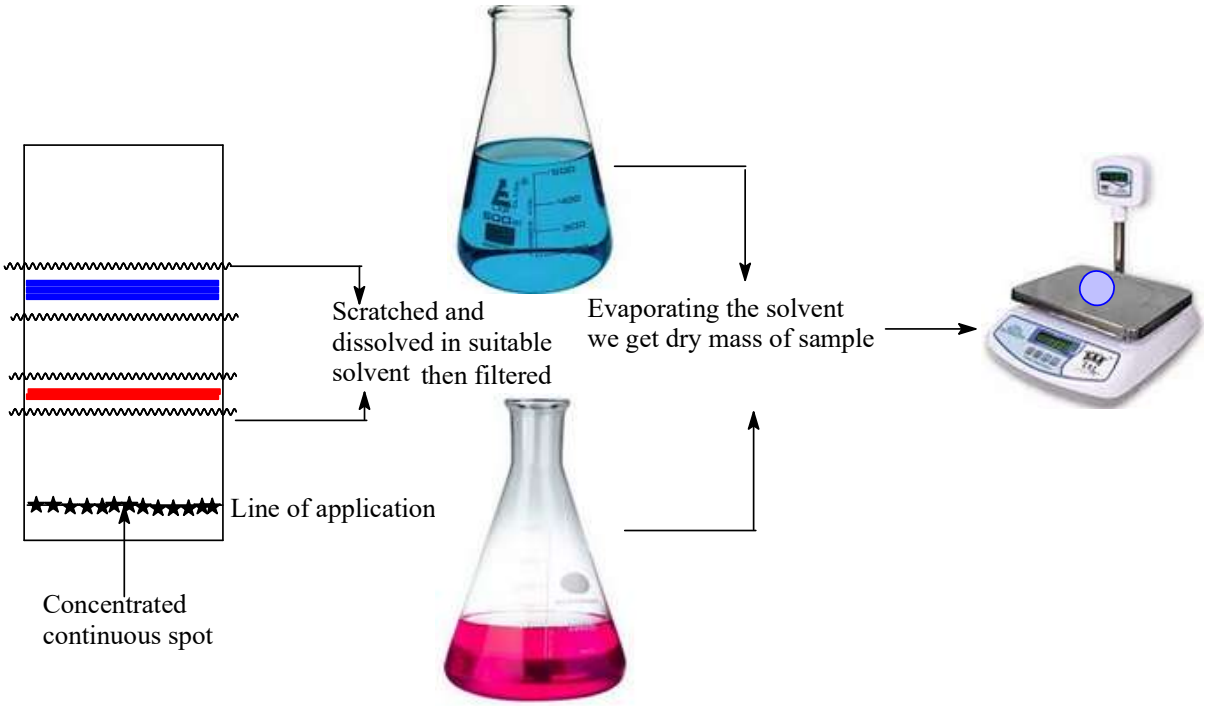


Fig 5.6 Processes of performing preparative TLC

Some time the components in amixture degrade during development or components have very close R_f values such situation create hurdle to identify the components. In order to separate the components in such situations 2D-TLC is performed in which the TLC plate is developed in two solvents with same or different polarity. For 2DTLC the square shaped TLC plates are prepared and spotting in 1^{st} development is done near the edge. After demarking first S.F. the plate is rotated by 90^0 and re developed in another mobile phase in which the components are separated well.The process of 2D-TLC can be understand by following Fig 5.7

Procedure for development of 2D TLC

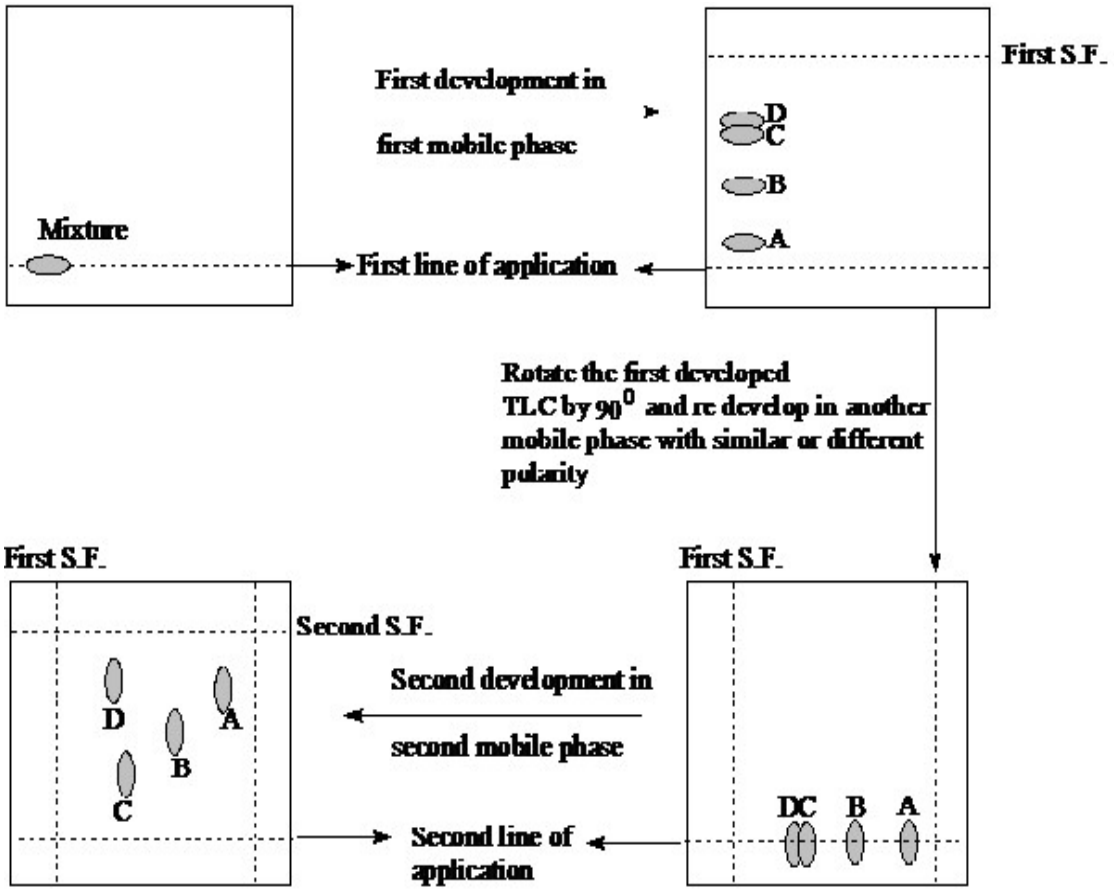


Fig 5.7 Procedure for development of 2D TLC

UNIT 5.4: SEPARATION GLUCOSE, FRUCTOSE AND SUCROSE ETC. IN THE GIVEN MIXTURE OF SUGARS

Principle: "*The differential migration of components of a mixture between ststionary and mobile phase as a result of attainment of equlibrioum is known as chromatography".* In present experiment the glucose and fructose in a mixture can be separated by chromatographic methods like paper chromatography or TLC. In order to separate the mixture by paper chromatography the following procedure is followed.

Requirement: To separate glucose and fructose by TLC and paper chromatography the following materials are required:

Stationary phase: Silica gel-G for TLC, Chromatographic paper for paper chromatography

Mobile phase: The following cocktails are used as mobile phase

[A] H_2O + saturated phenol +1% NH_4OH

[B] n- $CH_3CH_2CH_2CH_2OH$: CH_3COOH: H_2O [4:1:5 v/v] (upper layer)

[C] isopropanol :pyridine : H_2O : CH_3COOH [8:8:4:1 v/v]

TLC/Paper chromatographic chamber

Spray reagent: As a result of development visualization of spots is required to calculate R_f values for further analysis. For visualizing the developed paper/TLC plate the following reagents are required:

1. **A. Ammoniacal silver nitrate:** To prepare ammonical $AgNO_3$ solution add equal volumes of NH_4OH to a saturated solution of $AgNO_3$ and dilute with methanol to give a final concentration of 0.3M.After spraying the developed chromatograms,place it in an oven for 5-10 minutes, when the reducing sugars appear as brown spots.
2. **Alkaline permanganate**: Prepare aqueous solution of $KMNO_4$ (1%) containing 2 % Na_2CO_3.After spraying with this mixture, the chromatograms are kept at 100 °C for a few minutes, when the sugar spots appear as yellow spots in purple background.
3. **Aniline diphenylamine reagent**: Mix 5 volumes of 1% aniline and 5 volumes of 1% diphenylamine in acetone with 1 volume of 85% phosphoric acid. After spraying the dried chromatograms with this solution the spots are visualized by heating the paper at 100 °C for a few minutes.
4. **Resorcinol reagent**: Mix 1% ethanolic solution of resorcinol and 0.2N HCl (1:1 v/v).Spray the dried chromatograms and visualize spots by heating at 90 °C.
5. **Con.sulphuric acid**: Spraying the chromatogram with H_2SO_4 solution black spots are appeared due to charring of sugers.

Procedure: Put sufficient solvent (mobile phase) into the bottom of the Paper chromatographic/TLC chamber. Cover the lid and allow the chamber to be saturated with the vapours of mobile phase. Now take a sheet of whattman no. 1 chromatography paper (about 9 × 10 cm) or a TLC plate and place it on a piece of clean paper on a working table/bench. Draw a fine line with a pencil along the width of the paper and about 1.5cm from the lower edge. Do not mark TLC with pencil otherwise the silica will be removed mark on the side of TLC in order to ensure the line of application/spotting. Along this line place four equally spaced (about 2cm apart) small circles with a pencil (in paper only). Label the paper at the top with the name of each of the sugars and label the last unknown. Use a fine capillary to place the drops of the solutions of the sugars, glucose, fructose etc and the mixture. After spotting, dry the paper with hot air dryer for one minute, repeat this step again. Spotted TLC plate is dried by keeping it for few minutes at room temperature. Do not dry with air dryer in case of TLC. Place the spotted paper/ TLC plate in the solvent saturated chromatographic chamber and make the development by using the ascending technique. Close the tank with lid, allow the solvent to flow for about 30-45 minutes. Remove the paper/ TLC plate and immediately mark the position of the solvent front with a pencil. After the chromatogram has dried, spray the paper/TLC plate with the visualizing reagent. Put the paper on the hot plate at low temperature or expose it to the hot air dryer, until

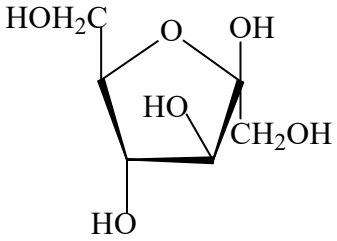
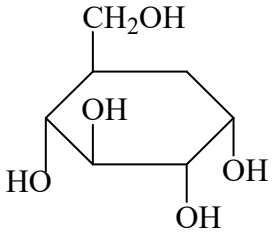
the colored spots appear.TLC plates can be dried in oven. The colors are stable for some weeks if kept in the dark and away from acid vapors. Circle the position of each spot with pencil. Calculate the R_f value for each spot and also for the spots the mixture contained by using the formula as given in Fig.5.4.

UNIT 5.5: R_f VALUE AND ITS DETERMINATION

When chromatographic paper or TLC plate is developed by allowing the mobile phase to run over stationary phase two forces comes in play. The propelling force, which drag the mobile phase against gravitational force due to capillary action and the second force force that pull back the mobile phase towards the line of application is known as retardation force. The retardation force is calculated by using the the following formula as also depicted in Fig 5.4.

$$R_f = \frac{\text{Distance travelled by spot/solute}}{\text{Distance travelled by mobile phase or simply solvent front (SF)}}$$

Observation: The following pattern of R_f value in different solvents can be achieved fig 5.8

Sugars	R_f values in different solvent system (Mobile Phase)		
	Solvent A	Solvent B	Solvent C
 Fructose	0.51	0.25	0.68
 Glucose	0.39	0.18	0.68

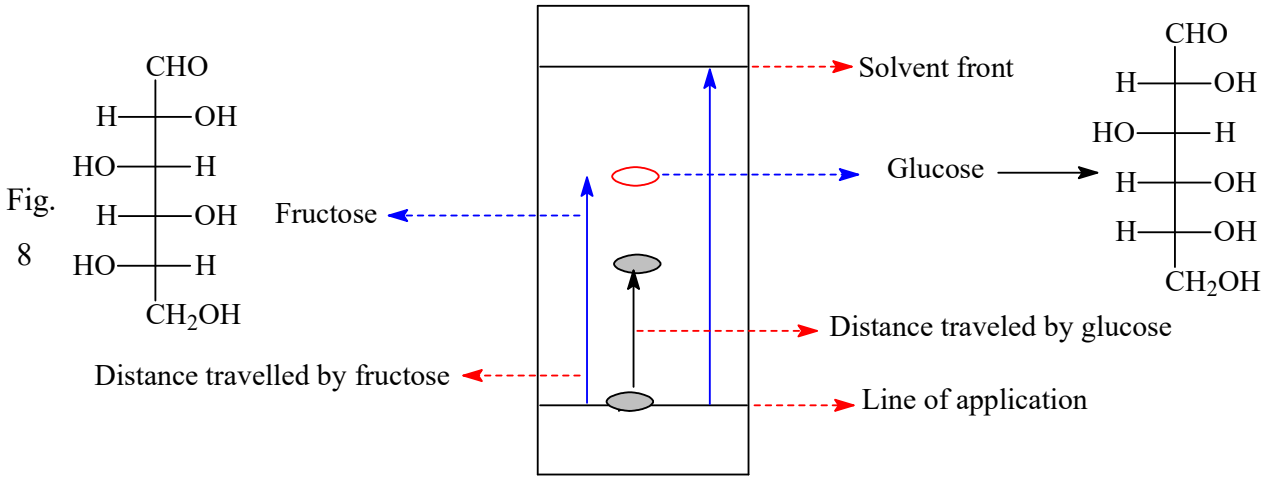


Fig 5.8 Separation pattern of glucose and fructose

Result: The R_f values of glucose and fructose in given mixture of monosaccharide are----------

-----respectively in different solvent systems/ mobile phases.

UNIT 5.6: SUMMARY

romatographyIn this unit we studied about the separation technique like ch. The basic concept about chromatography with its history has been discussed. atography based on type of chrom interaction of solute with mobile and stationary phase has been discussed. Partition chromatography like paper chromatography alongwith its different developmental procedures have been discussed like ascending, per chromatography etcdescending and circular pa. The procedure for TLC has also been discussed in detail. Rf value and its determination is being described in this unit. Analytical and preparative alongwith2D- TLC will make aware the students that in whicht these techniquescondition we can selec . The Detailed experimental procedure for the separation of mixture of monosaccharidesglucose and fructose by ppaper chromatography/ thas been described in this uni TLC.

UNIT 5.7: TERMINAL QUESTIONS

Q .1. MCQs.

ptionChoose the correct o :

i The term chromatography was coined by

[A] M.Tswett [B] Synge

[C] Krickland [D] Sthall

ii. Paper chromatography is an example of:

[A] Adsorption [B] Partition

[C]Sorption]D [Size exclusion

iii. In silica gel-G, G stands for:

[A] Graphite]G [Gravitation

[C] Gypsium]D [Simply for gel

iv. TLC is:

[A] Partition chromatography [B] Electrical mobility of ionic species

[C] Sorption chromatography [D]Adsorption chromatography

v. electrophorosis involves A combination of paper chromatography and:

[A] Partition chromatography [B] Electrical mobility of ionic species

[C] Both A and B [D] none of them

vi. Pattern on paper in chromatography is called

[A] Chroming [B] Chroma

[C] Chromatogram [D] Chromatograph

vii. Components which have small value of K have affinity for

[A] Mobile phase [B] Stationary phase

[C] no phase [D] Solution

viii. Chromatography is used to separate

[A] Mixture [B] Solution]

[C] Molecules [D] Atoms

ix. Mobile phase can be

[A] Gas only [B] Liquid only

[C] Solid or liquid [D] Gas and liquid

x. For quantitative analysis which of the following technique in chromatography is useful ?

[A] Preparative TLC [B] Analytical TLC

[C] Analytical HPLC [C] 2D- paper chromatography

Q.2. What is chromatography? How it is classified? Discuss briefly

Q.3. How will you differentiate among the term Chromatograph, Chromatogram, Chromatography and Chromatographer?

Q.4. Why 2D-TLC is performed? Discuss briefly.

Q.5. What are spraying agents? Why these are required in chromatography?

Q.6. Why TLC chamber is saturated with mobile phase?

Q.7. What is partition coefficient?

Q.8. Define retardation factor

Q.9. How alanytical chromatography differs from preparative chromatography?

Q.10. What are different sequential steps involved in paper chromatography?

UNIT 5.8: ANSWERS OF TERMINAL QUESTIONS:

i	A	ii	B	iii	C	iv	D	v	C
vi	C	vii	B	viii	A	ix	D	x	A

UNIT 5.9: REFERENCES:

James M Bobbitt, Arthur E Schwarting, Roy J. Gritter 1968. Introduction to Chromatography Van Nostrand Reinhold Company, New York