

B.Sc. (Hons) Part II

Paper — Physical Chemistry  
Topic — Chemical Kinetics

Dr. Om Prakash Singh  
Department of Chemistry,  
Maharaja College, Ara.

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Experimental Measurements of Order in :-

A. Acid Catalysed Hydrolysis of Methyl Acetate :-

Methyl acetate undergoes hydrolysis in the presence of a mineral acid which acts as a catalyst to give acetic acid and methyl alcohol. The reaction is given by as



The rate of this reaction is given by

$$\frac{dx}{dt} = k' [CH_3COOCH_3] [H_2O]$$

This is a bimolecular reaction, i.e. it involves two molecules. But, since water is present in large excess, its active mass (molar concentration) virtually remains constant (unchanged) during the course of the reaction. Therefore, its active mass gets included in the constant, and the above reaction reduces to :

$$\frac{dx}{dt} = k [CH_3COOCH_3]$$

Thus, the rate of the reaction is determined by one concentration term only (i.e. by a single power of the concentration term only). The rate of this reaction is determined only by the concentration of the methyl acetate.

Hence, the reaction is of the first order and

obeys first order rate equation. Reactions of this type are also known as pseudo first order reactions, or pseudo unimolecular reactions.

This reaction is studied as follows:

The reaction mixture contains methyl acetate dissolved in water and a small quantity of HCl which acts as a catalyst. This hydrolysis gives acetic acid and methyl alcohol.

As acetic acid is produced during the reaction, the progress of the reaction can be measured by withdrawing a definite volume of the reaction mixture at definite intervals of time and titrating the acetic acid formed with a standard solution of NaOH. The amount of alkali used is equivalent to the total amount of hydrochloric acid present originally and the amount of acetic acid formed in the reaction. At the start of the experiment (i.e.  $t=0$ ), the amount of HCl added is determined by titrating the reaction mixture. If  $V_0$  is the volume of alkali to neutralise HCl at the start of the reaction and  $V_t$  the volume after time  $t$ , then  $(V_t - V_0)$  will be the volume required to neutralise acetic acid formed at time  $t$ . This amount (i.e.  $V_t - V_0$ ) will be identical with  $x$  in the rate equation for the first order because the amount of acetic acid formed at any time  $t$  is equivalent to the amount of methyl acetate decomposed at that time. The final reading is usually taken after 24 hours or more. When the reaction is complete,  $V_{\infty}$  be the volume of alkali required to neutralise the reaction mixture (i.e. here the solution mixture contains HCl

and the amount-acetic acid formed). Thus, this amount-of acetic acid formed at the end of the reaction will be equivalent to the initial concentration (a) of the methyl acetate and will be proportional to  $(V_{\infty} - V_0)$ . Now, the concentration of methyl acetate at any time t (i.e. a-x) will be proportional to  $\{(V_{\infty} - V_0) - (V_t - V_0)\} = (V_{\infty} - V_t)$ .

The first-order rate expression is given by as:

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

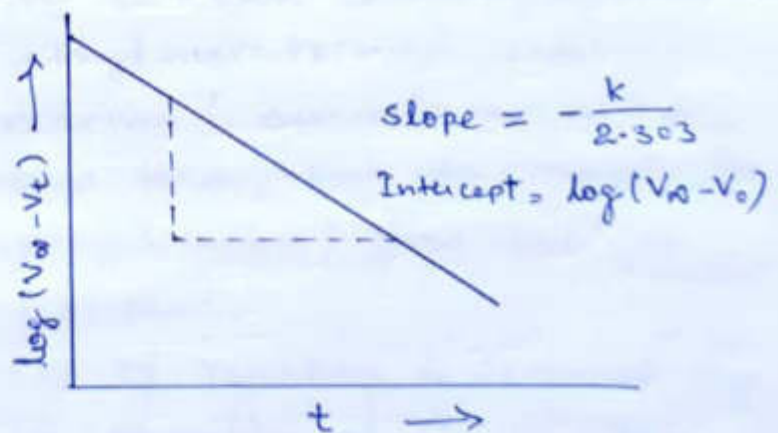
which can now be expressed as

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

Hence, the value of rate constant (k) can be calculated.

when we plot  $\log (V_{\infty} - V_t)$  versus time (t), a straight-line with negative slope will be obtained as follows:

From the slope, k can be calculated.



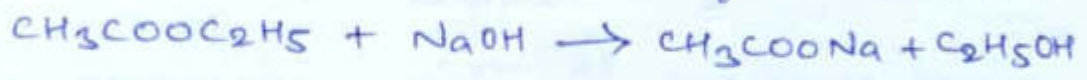
Thus one can report the theoretical and graphical values of rate constant (k).

### B. Saponification of Ester :-

The process of making soaps is called saponification. Soaps are just potassium or sodium salts of long-chain fatty acids. During saponification, an ester reacts with strong inorganic base to produce alcohol and soap. In

general, saponification is the hydrolysis of an ester with NaOH or KOH to give alcohol and sodium or potassium salt of the acid.

There are many reactions of saponification of esters. A typical example of these is the acid catalysed (HCl) hydrolysis or saponification of ethyl acetate with NaOH. The reaction takes place as given below:



The rate of this reaction is given by

$$\frac{dx}{dt} = k [CH_3COOC_2H_5] [NaOH]$$

This is a typical second order reaction. Its molecularity is also equal to 2. The rate of the reaction is determined by taking into account of both concentration terms.

The reaction is studied as follows:

The reaction mixture contains equimolar concentrations of ethyl acetate and sodium hydroxide. The reaction is carried out at a constant temperature throughout the process. The hydrolysis (or saponification) gives sodium acetate and ethyl alcohol.

The course of reaction is followed by removing a definite quantity of the reaction mixture at various times and titrated against a standard acid to know the concentration of NaOH left behind. It is clear from the reaction that the concentration of NaOH will decrease with increase in the reaction time. Thus, the volume of the acid used is a measure of concentration of NaOH or ester.

The volume of the acid used when  $t = 0$ , gives the initial concentration (a) of the reactants. The volume of the acid consumed at any time  $t$  will

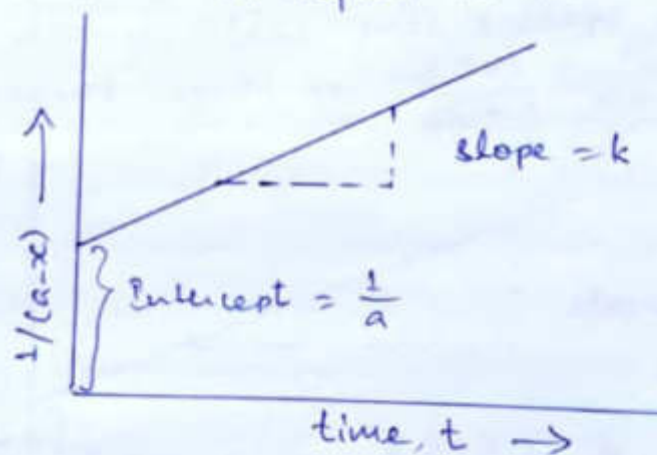
give  $(a-x)$ , i.e. the amount of unreacted NaOH or ethyl acetate at any time  $t$ . The value of  $x$  can then be calculated.

The second order rate equation is given by as :

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

This expression is valid <sup>only</sup> for reactants having equal concentrations. The rate constant,  $k$  can be determined by substituting the values of  $a$ ,  $x$  and  $(a-x)$  at different time spans in the above equation.

Again, if we plot  $1/(a-x)$  versus time  $t$ , a straight line will be obtained with a slope equal to  $k$  and intercept equal to  $1/a$ .



Thus one can report the theoretical and graphical values of rate constant ( $k$ ).

Furthermore, if we take different initial concentrations of reactants, then another rate expression for second order reaction is applied. Let  $a$  and  $b$  be the initial concentrations of ethyl acetate and sodium hydroxide respectively. The course of reaction is followed by withdrawing a definite volume of reaction mixture from time to time and titrating with standard acid to get the concentration of unconsumed NaOH. If  $x$  is the decrease in

(17)  
 concentration of NaOH at any time  $t$ , then  $(b-x)$  will be the amount of unreacted NaOH at time  $t$ . Similarly  $(a-x)$  will be the amount of unreacted ester at time  $t$ . Now by using the second order rate expression given by

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

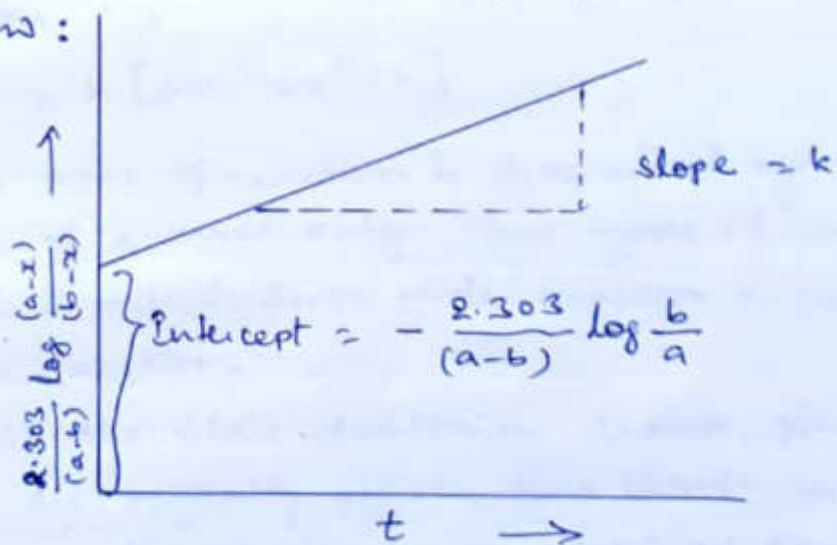
$$\begin{cases} (a-x) - (b-x) \\ = a-x-b+x \\ = (a-b) \end{cases}$$

and putting the values of  $a$ ,  $b$ ,  $(a-b)$ ,  $(a-x)$  and  $(b-x)$  we can calculate the values of  $k$  at different  $t$  values.

Rearranging the above equation we have

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

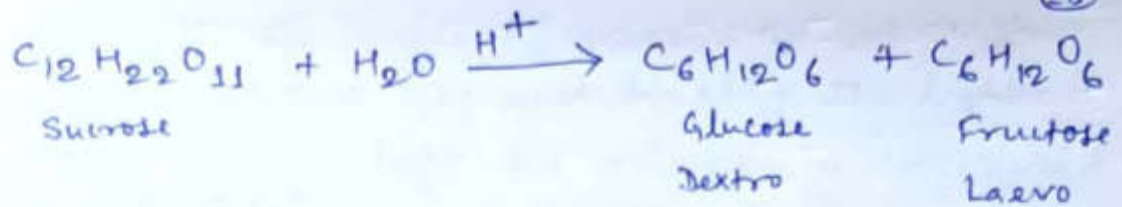
This is similar to an equation for a straight-line. So, the plot between  $\frac{2.303}{(a-b)} \log \frac{(a-x)}{(b-x)}$  versus  $t$  should be a straight-line with a slope equal to  $k$  and intercept equal to  $-\frac{2.303}{(a-b)} \log \frac{b}{a}$  as shown below:



Thus, we can report the theoretical and graphical values of rate constant for the saponification of ethyl acetate.

### C. Inversion of Cane Sugar :-

The inversion of cane sugar is the chemical conversion of sucrose in solution into glucose and fructose. The reaction is



The rate of reaction between sucrose and water catalysed by hydrogen ion ( $\text{H}^+$  in  $\text{HCl}$ ) is followed by measuring the angle of rotation of polarized light passing through the solution. The progress of the reaction can be observed by measuring the change in angle of rotation by means of a polarimeter.

The rate of reaction for the inversion of sucrose is

$$\frac{dx}{dt} = k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}]$$

It is a bimolecular reaction. But the water is present in such large excess that its concentration does not change appreciably (i.e. remains constant), and the reaction follows the equation for a first order reaction. i.e.

$$\frac{dx}{dt} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

Thus, the rate of reaction is determined by the concentration of sucrose only. This type of reaction is also called pseudo first order reaction or pseudo unimolecular reaction.

As all the three substances, sucrose, glucose and fructose are optically active, this change in rotation is proportional to the amount of the sugar decomposed.

Sucrose is dextrorotatory, but the resulting mixture of glucose and fructose is slightly levorotatory, because the levorotatory fructose has a greater molar rotation than the dextrorotatory glucose. As the sucrose is used up and the glucose-fructose mixture

(19)

is formed, the angle of rotation to the right becomes less and less, and finally the light is rotated to the left. The rotation is determined at the beginning and at the end of the reaction, the difference between these two readings will be the measure of the original concentration of sucrose.

Let  $\alpha_0$  and  $\alpha_\infty$  be the angles of rotation at the beginning (i.e. at  $t=0$ ) and when the reaction is complete respectively, and  $\alpha_t$  is the angle at any time  $t$ . Then  $(\alpha_0 - \alpha_\infty)$  is proportional to the initial concentration of sucrose, i.e.  $a$ , and  $(\alpha_0 - \alpha_t)$  is proportional to the amount of sucrose inverted at any time  $t$ , i.e.  $x$ . So, the amount of sucrose left behind at time  $t$ , i.e.  $(a-x)$  will be  $(\alpha_0 - \alpha_\infty) - (\alpha_0 - \alpha_t) = (\alpha_t - \alpha_\infty)$ .

Now, the first-order rate expression is given by as:

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

On putting the values of  $a$  and  $(a-x)$ , the rate equation becomes

$$k = \frac{2.303}{t} \log \frac{(\alpha_0 - \alpha_\infty)}{(\alpha_t - \alpha_\infty)}$$

And hence, the value of rate constant can be calculated.

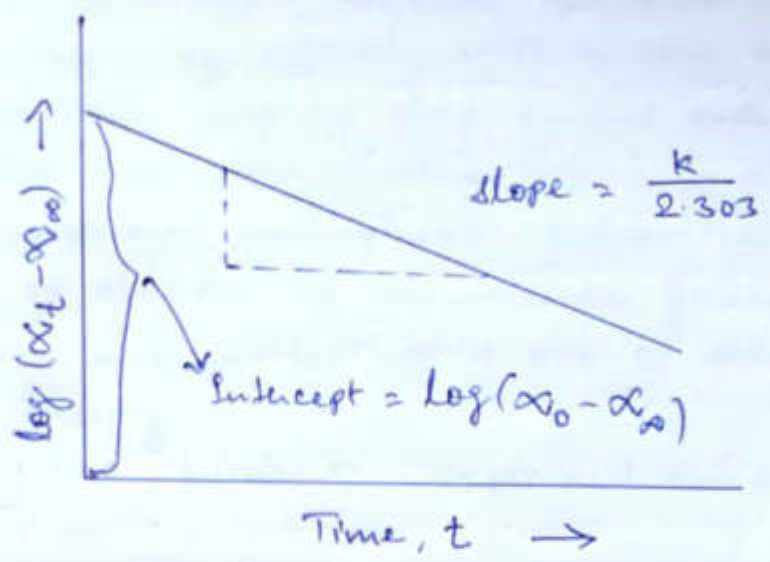
Further, the above equation can be rearranged as:

$$\log (\alpha_t - \alpha_\infty) = -\frac{k}{2.303} \cdot t + \log (\alpha_0 - \alpha_\infty)$$

Comparing it with the equation of straight line (i.e.  $y = mx + c$ ), it suggests that a plot of  $\log (\alpha_t - \alpha_\infty)$  versus time,  $t$  will give a straight line with a negative slope  $k/2.303$  and an intercept  $\log (\alpha_0 - \alpha_\infty)$ . From the slope we can



calculate the value of rate constant, k.



Therefore, we can report the theoretical as well as graphical values of rate constants for the inversion of cane sugar.

### First Order Gas Phase Reaction (LINDEMANN THEORY)

This is also known as the theories of unimolecular gaseous reactions.

Unimolecular reactions are the reactions in which activated complex is formed from a single reactant molecule and are of the first order under certain conditions.

According to the collision theory, for chemical reactions to occur, there must be collisions between the reactant molecules. In a bimolecular reaction, for example, when two molecules A and B collide, their relative kinetic energy exceeds the threshold energy resulting breaking and formation of bonds. It means that the reaction should follow the second order kinetics. But what will be the mechanism of a unimolecular reaction?

For a reaction of the type:



the molecule A should acquire the necessary activation energy by colliding with another molecule, then the reaction should obey second order kinetics and not the first-order kinetics which is actually observed in several unimolecular gaseous reactions. A number of theories of unimolecular gaseous reactions have been put forth and one of them is Lindemann Theory.

In 1922, Lindemann explained this anomaly and suggested that - :

(i) In unimolecular reaction, reactant molecules are activated by collisions with one another. Some of the molecules may possess sufficient energy to pass into the final products without receiving additional energy. Such molecules are usually termed as energised or activated molecules.

(ii) If the rate of activated molecules to yield products is low as compared to the  $\frac{\text{rate}}{\text{with}}$  which activated molecules deactivate by collision, a stationary concentration of activated molecules may be formed.

As the activated molecules are in equilibrium with the normal molecules, the concentration of activated molecules will be proportional to that of normal molecules. It, therefore, follows that - the rate of the reaction is proportional to the concentration of activated molecules which in turn is proportional to the  $\frac{\text{first-}}$  power of concentration of normal molecules as the two are in equilibrium with each other. It means that - the reaction is of the first-order.

(iii) At low pressures, the collisions can not maintain a supply of activated molecules. Therefore, the rate of the reaction will depend upon the rate of activation and hence is proportional to the

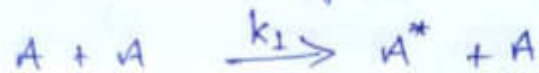
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square of the concentration of reacting molecules. Thus, the reaction becomes of the second order at low pressures.

### Mathematical formulation of Lindemann's Theory :-

In a unimolecular reaction,  $A \rightarrow P$ , it follows the mechanism given by as

(a) Activation by collisions :- The process of energization by collision is represented by

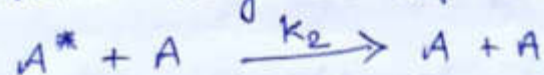


where  $A$  is a normal molecule and  $A^*$  is an activated molecule which possesses sufficient energy to pass into the products. Here

$$\text{Rate of activation} = k_1 [A]^2$$

where  $k_1$  is the specific rate constant for the second order reaction.

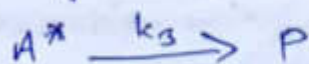
(b) Deactivation by collisions :- The process of deactivation may be represented as



$$\text{Here, Rate of deactivation} = k_2 [A^*] [A]$$

where the rate of deactivation is slow as compared to the rate of activation and the reaction should be second order.

(c) Decomposition :- The decomposition of activated molecules may be represented as



$$\text{Here, rate of decomposition} = k_3 [A^*]$$

where  $k_3$  is the first order rate constant.

As the concentration of  $A^*$  is so small that it is not changing with time, it means that

$$\frac{d[A^*]}{dt} = 0$$

— (1)

But the overall rate of formation of  $A^*$  is given by,

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A^*][A] - k_3[A^*] \quad \text{--- (2)}$$

$$\text{or } 0 = k_1[A]^2 - k_2[A^*][A] - k_3[A^*]$$

$$\text{or } k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$$

$$= [A^*] \{ k_2[A] + k_3 \}$$

$$\text{or } [A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad \text{--- (3)}$$

But the rate of reaction will be proportional to the concentration of the activated molecules, i.e.

$$\text{Rate} = -\frac{d[A]}{dt} = k_3[A^*] \quad \text{--- (4)}$$

On putting the value of  $[A^*]$  from eq. (3) in eq. (4) we get-

$$\text{Rate} = r = \frac{k_1 \cdot k_3 [A]^2}{k_2[A] + k_3} \quad \text{--- (5)}$$

Here we see that the rate law of equation (5) has no definite order (i.e. of mixed order). But if we consider two limiting cases as given below:

(i) At high Pressure: At high pressure /  $k_2[A] \gg k_3$ , the rate of deactivation will be dominant, and then the term  $k_3$  in the denominator can be neglected and we get-

$$r = \frac{k_1 k_3 [A]^2}{k_2 [A]} = k' [A] \quad \text{--- (6)}$$

Here, the reaction is of the first-order.

(ii) At low Pressure: At low pressure /  $k_3 \gg k_2[A]$ , the rate of decomposition will be dominant, so then the term  $k_2[A]$  in the denominator can be neglected and then

$$r = \frac{k_1 k_3 [A]^2}{k_3} = k_1 [A]^2 \quad \text{--- (7)}$$

Here, the reaction is of the second order.

Thus the equation (5) predicts that a unimolecular reaction can either be of first-order or second order depending on which of the two terms in the denominator is larger.

The first-order rate coefficient  $k$  found experimentally is defined as

$$r = k[A] \quad \text{--- (8)}$$

Now from equation (5) and (8) we have

$$k[A] = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3}$$

$$\text{or } k = \frac{k_1 k_3 [A]}{k_2 [A] + k_3}$$

$$\text{or } k = \frac{\frac{k_1 k_3}{k_2}}{1 + \frac{k_3}{k_2 [A]}} \quad \text{--- (9)}$$

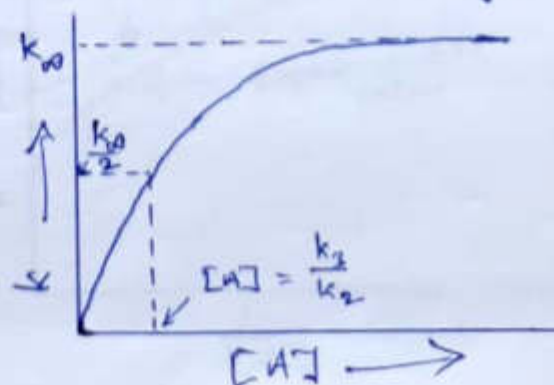
$$\text{or } k = \frac{k_0}{1 + \frac{k_3}{k_2 [A]}} \quad \text{--- (10)}$$

where  $k_0 = k_1 k_3 / k_2$

### Limitations of Lindemann Theory :-

Although this theory gives a satisfactory qualitative interpretation of unimolecular reactions, yet quantitatively it is not completely satisfactory, and, therefore, certain modifications are required.

According to equation (10), the plot of the first-order rate constant  $k$  versus  $[A]$  is a hyperbola. The



rate constant-  $k$  is a constant- in the higher concentration range but- falls off at- lower concentrations. From the plot- (and also from the eq<sup>n</sup> (10)) we see that- when  $k_2[A] = k_3$ , then  $k = \frac{k_{\infty}}{2}$ . We can write the concentration at which this is true as  $[A]_{1/2}$ . Thus

$$[A]_{1/2} = \frac{k_3}{k_2} = \frac{k_{\infty}}{k} \quad \text{--- (11)}$$

Application of this relationship to experimental data raises some difficulties. The value of  $k_{\infty}$  is an experimental quantity. However, it has been found experimentally that the values of  $[A]_{1/2}$  were always smaller than the estimated values. Thus it is concluded that- the error must lie in the estimation of  $k$  rather than  $k_{\infty}$  because  $k_{\infty}$  is an experimental quantity and a modification in the Lindemann theory is necessary.

Another difficulty with the Lindemann mechanism becomes evident- when experimental results are plotted in another way. The equation (9) after rearranging can be written as

$$\frac{1}{k} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1 [A]}$$

A plot of  $1/k$  versus  $1/[A]$  should give a straight-line. However, deviations from linearity have been found as illustrated in the figure given below.

