B.Sc. (Hons) Part II

CHEMICAL KINETICS

Paper : III A Physical Chemistry

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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:

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

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 accounts 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.

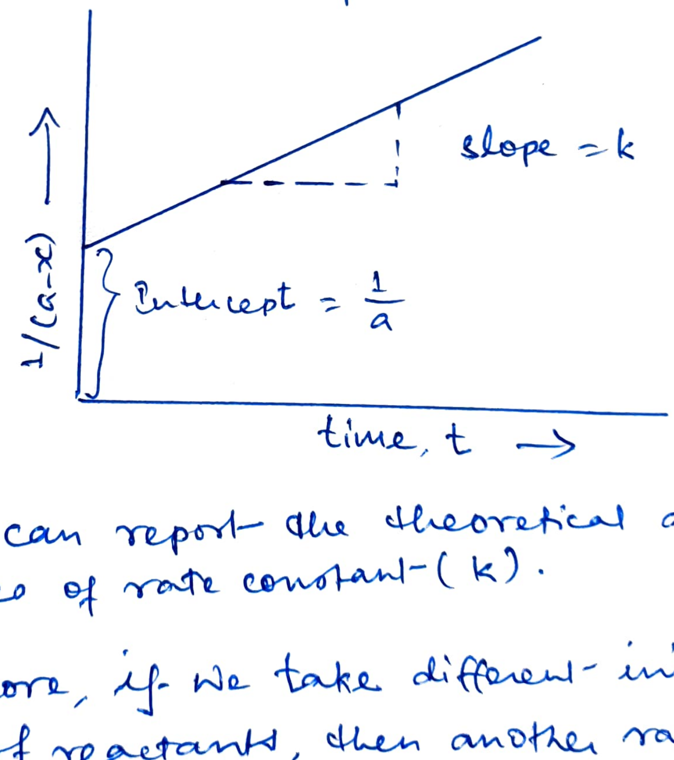
The volume of the acid used when $t=0$, gives the initial concentration (a) of the reactants. The volume of the acid consumed at any time t will give (a−x), i.e. the amount of unreacted NaOH or ethyl acetate at any time t. The value of x can then be calculated.

The second order rate equation is given by as:

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

This expression is valid only 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 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

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

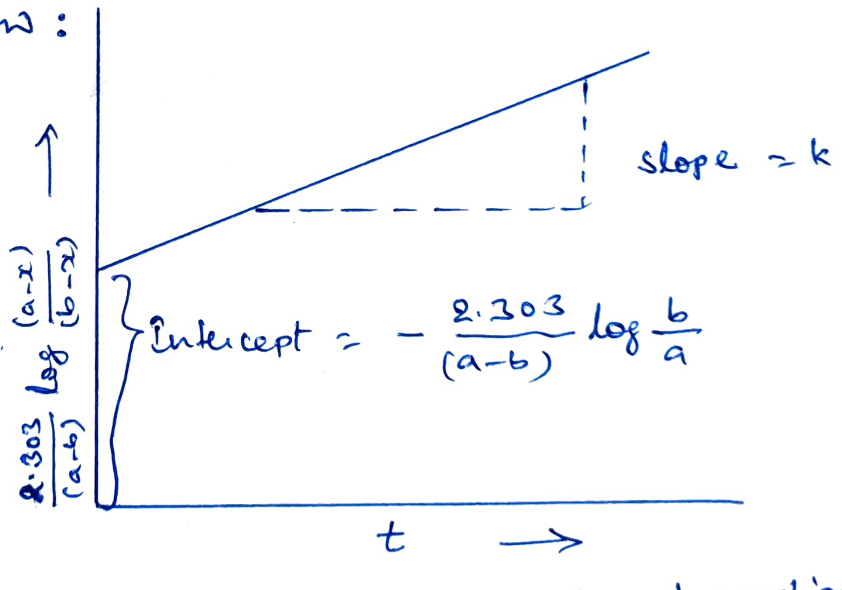
$(a-x)-(b-x)$
$= a-x-b+x$
$= (a-b)$

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

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

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.

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