

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 MethylAcetate :-

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

$$\frac{dx}{dt} = k' [\text{CH}_3\text{COOCH}_3] [\text{H}_2\text{O}]$$

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 :

$$\frac{dx}{dt} = k [\text{CH}_3\text{COOCH}_3]$$

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:

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

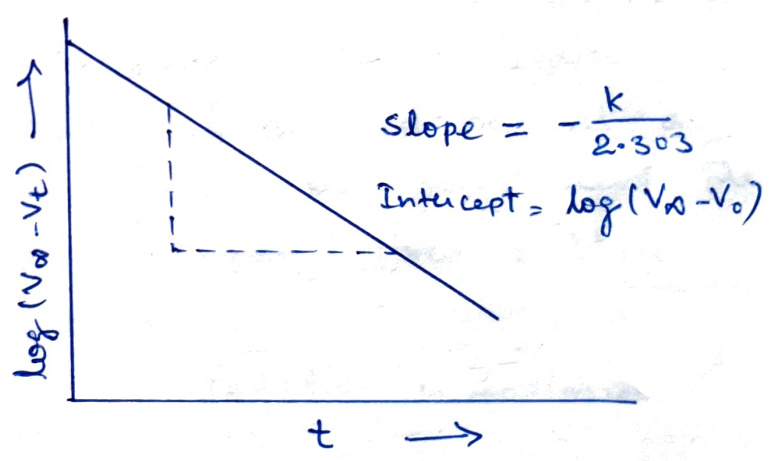
which can now be expressed as

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

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).

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