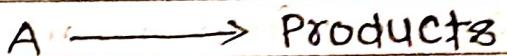


Class \Rightarrow B.Sc.(Hons.) Part ISubject \Rightarrow ChemistryChapter \Rightarrow Chemical KineticsTopic \Rightarrow First order reactionName \Rightarrow Dr. Amarendra Kumar
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First order reaction

A reaction is said to be of the first order if the rate of the reaction depends upon one concentration term only.

Let us consider a first order reaction



Suppose that at the beginning of the reaction, $t=0$, the concentration of A is a moles per litre.

If after time t , x moles of A have changed, the concentration of A is $a-x$.

Then the first order reaction, the rate of reaction, dx/dt is directly proportional to the concentration of the reactant.

Thus,

$$\frac{dx}{dt} \propto (a-x)$$

$$\text{or } \frac{dx}{dt} = K(a-x)$$

Where K is called the rate constant or the specific reaction rate for the reaction of the first order.

$$\frac{dx}{a-x} = K dt \quad ①$$

Integration of the expression ① gives

(2)

$$\int \frac{dx}{a-x} = \int k dt$$

$$\text{or } -\ln(a-x) = kt + I \quad (2)$$

Where I is the constant of integration.

The constant K may be evaluated by putting $t=0$ and $x=0$.

Thus,

$$I = -\ln a$$

Substituting this value in equation (2) we get

$$-\ln(a-x) = kt + (-\ln a)$$

$$\text{or } \frac{\ln a}{a-x} = kt \quad (3)$$

$$\text{or } K = \frac{1}{t} \ln \frac{a}{a-x}$$

Changing into common logarithms

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \quad (4)$$

This equation is called the first order reaction.

Sometimes the integrated rate law in the following form is also used.

$$K = \frac{2.303}{t_2 - t_1} \log \frac{(a-x_1)}{(a-x_2)}$$

Where x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.

units of First order Rate Constant

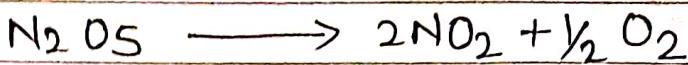
The rate constant for the first order reaction is independent of the concentration. It has the unit

time⁻¹.

(3)

Examples of first order reaction

- ① Decomposition of N_2O_5 in CCl_4 solution \Rightarrow



If V_t the volume of O_2 at any time t and V_0 the final volume of oxygen when the reaction is completed. The V_0 is a measure of the initial conc. of N_2O_5 and $(V_0 - V_t)$ is a measure of undecomposed N_2O_5 ($a-x$) remaining at time t . Thus,

$$K = \frac{2.303}{t} \log_{10} \frac{V_0}{V_0 - V_t}$$

Putting the value of V_0 & $(V_0 - V_t)$ at different intervals t . The value of K is found to be constant. Thus, it is a reaction of the first order.

- ② Decomposition of Benzene diazonium chloride ($C_6H_5N=NCl$) in Water \Rightarrow



Let V_0 be the volume of N_2 measured at the end of the reaction and ~~volume~~ V_t be the volume at any time t , then

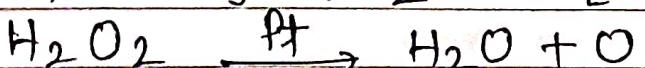
$$\begin{aligned} a &\propto V_0 \\ (a-x) &\propto (V_0 - V_t) \end{aligned}$$

Substituting the values of a and $(a-x)$ in the first order reaction, we get

$$K = \frac{2.303}{t} \log \frac{V_0}{V_0 - V_t}$$

The value of K is found to be constant, thus Thus, it a first order reaction.

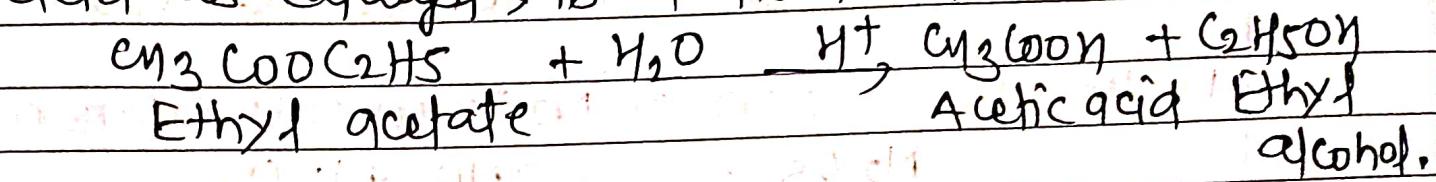
- ③ Decomposition of H_2O_2 in aqueous soln.



- ④ Hydrolysis of an ester i.e. Ethyl acetate or methyl acetate in the presence of a mineral

4

acid as catalyst, is a first order reaction.



⑤ Inversion of cane sugar (sucrose) is catalysed with dil. HCl is a first order reaction.

