

Class → B Sem (A.S.) Part I

Subject → Chemistry

Chapter → Chemical Kinetics

Topic → First order reaction

Name → Dr. Amarendra Kumar

Dept. of Chemistry

Jain College, Ara.

## 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,

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

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

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

$$t=0 \text{ and } x=0$$

Thus,

$$I = -\ln a$$

Substituting this value in equation (2) we get

$$-\ln(a-x) = kt + (-\ln a) \quad (3)$$

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

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

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

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<sup>-1</sup>

(3)

## Examples of first order reaction

### ① Decomposition of $\text{N}_2\text{O}_5$ in $\text{CCl}_4$ solution $\Rightarrow$



If  $V_t$  the volume of  $\text{O}_2$  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  $\text{N}_2\text{O}_5$  and  $(V_0 - V_t)$  is a measure of undecomposed  $\text{N}_2\text{O}_5$  ( $q - x$ ) remaining at time  $t$ . Thus,

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

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 ( $\text{C}_6\text{H}_5\text{N}=\text{NCl}$ ) in water $\Rightarrow$



Let  $V_0$  be the volume of  $\text{N}_2$  measured at the end of the reaction and ~~volume~~  $V_t$  be the volume at any time  $t$ , then

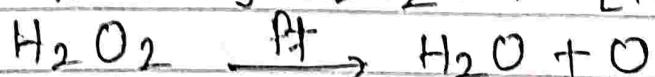
$$\begin{aligned} q &\propto V_0 \\ (q-x) &\propto (V_0 - V_t) \end{aligned}$$

Substituting the values of  $q$  and  $(q-x)$  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. This thus, is a first order reaction.

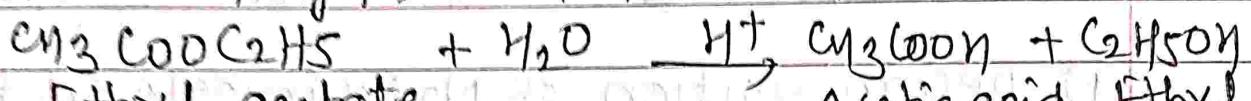
### ③ Decomposition of $\text{H}_2\text{O}_2$ in aqueous soln.



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

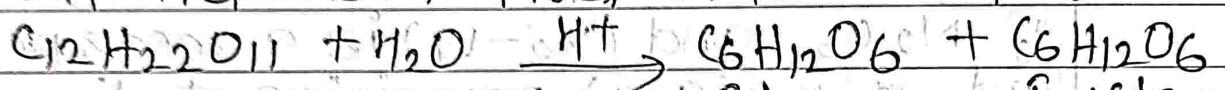
(4)

acid as catalyst, is a first order reaction.



Ethyl acetate      Acetic acid      Ethyl alcohol.

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



Glycose      Fructose

(Dextro-beta-(laevio-alpha)-fractose)