CHEMISTRY
CLASS - XII

Chapter : Chemical Kinetics

1. If a reaction is of zero order, will its molecularity be zero?

Ans. Case I:

Any elementary reaction has a definite order and molecularity that are positive integers (< 4 on the ground of probability). Therefore the above statement does not apply to elementary reactions.

Case II:

Complex reactions comprise of several elementary steps and therefore the notion of molecularity does not apply to such multistep reactions. Moreover, the notion of order may not apply to such reactions. If a complex reaction does have an order, i.e., if a simple rate expression is established experimentally, then it may so happen in some cases that the reaction is zero order with respect to a particular reactant. This means that the rate-determining step in the complex sequence of reactions does not involve the particular reactant. Therefore it can be said that zero order reactions are all complex reactions where the notion of molecularity does not apply.

Case III:

Under certain specific conditions, decomposition of certain gases on specific solid surfaces are observed to be zero order at the high pressure limit. In these cases the reaction centres on the solid surfaces become saturated with the adsorbed gaseous reactant species and the rate of overall reaction is not noticeably affected by a small increase or decrease in the reactant concentration. Under these conditions the reaction effectively becomes a zero order reaction with respect to the reactant species, but the molecularity of the overall reaction, comprising of several steps, does not exist.

2. Show that for a first order reaction $\mathbf{a - x = a\left(\frac{1}{2}\right)^{\frac{t}{t_{\frac{1}{2}}}}}$.

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$$ln\left(\frac{a}{a-x}\right) = kt$$

$$or,\ \frac{a}{a-x} = e^{kt}$$

$$or,\ a - x = ae^{-kt}$$

$$or,\ a - x = ae^{\frac{-0.693}{t_{\frac{1}{2}}}t}$$

$$or,\ a - x = a\left(e^{-0.693}\right)^{\frac{t}{t_{\frac{1}{2}}}}$$

$$or,\ a - x = a\left(\frac{1}{2}\right)^{\frac{t}{t_{\frac{1}{2}}}}$$

3. Show that a first order reaction becomes complete only at infinite time.

Ans. From the integrated rate equation $a=a_0e^{-kt}$, it appears that concentration of the reactant would become zero only when an infinite time is given. However, there is a logical flaw in such a question because the continuous limit approximation used to derive this expression breaks down when the number of reactant molecules becomes small. This means that when many billions of reactant molecules are present, the decrease in the number of reactant molecules at a particular instant is negligible in comparison with the total number of reactant molecules. Under these conditions, the number of molecules may be taken as a continuous variable although in a strict sense, it is a discrete variable. When the number of reactant molecules becomes small this mathematical model and conclusions reached from it become untenable. In that case, a different statistical model is applied where the number of molecules is taken as a discrete variable but the probability of reaction varies continuously with time.