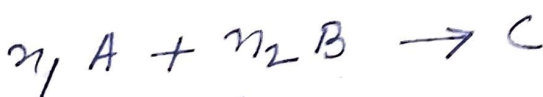


Rate Law and Rate Constant :-

A reaction is occur when reactant molecules collide each other. So the rate of a reaction depends on the collision among the reactant molecule in a unit space and unit time. And the number of collision increase with increase of reactant molecules in that unit space. So at the beginning of a reaction reaction rate is higher when time passes number of reactant molecule decline and rate of the reaction decreases.

Thus rate of a reaction is found experimentally to be proportional to the concentration of reactants to a proper power.

such as -



$$\text{Rate} = k C_A^\alpha C_B^\beta$$

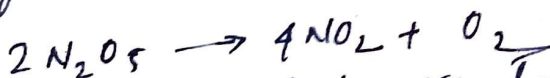
$$\text{or Rate} = -\frac{1}{n_1} \frac{dA}{dt} = k C_A^\alpha C_B^\beta \quad \text{--- (i)}$$

Where k is rate constant and eqn (i) is to be called rate law.

Order and molecularity :-

Rate of a reaction is nothing but the power of concentration terms in rate equation. Thus in above equation (i) the order is α with respect of 'A' and β with respect of 'B' and the ~~order~~ overall ~~order~~ order of the reaction $\alpha + \beta$.

Order is purely experimentally determined character which have no relation with the stoichiometry of a reaction. eg



Though the stoichiometry of the reactant is 2 but its order is one. Order may be zero or fraction also and (-)ve also. Reaction having order more than three is rare.

Molecularity is a theoretical concept, it signify the number of species (atom, molecule, ion or radical) involved to form product. For elementary reaction, (single step reaction) stoichiometry represents molecularity but for complex reaction where intermediate involve, it is difficult to calculate molecularity.

Molecularity can't be zero, (-)ve or fraction.

First Order Reaction:

Let a reaction follows 1st order kinetics



where 'n' coefficient of A.

$$\text{So rate} = -\frac{1}{n} \frac{d[A]}{dt}$$

According to rate law $\text{rate} \propto [A]$

$$-\frac{1}{n} \frac{d[A]}{dt} = k[A]$$

$$\text{or } -\frac{d[A]}{dt} = nK[A]$$

$$\text{or } -\frac{d[A]}{dt} = K_{obs}[A]$$

$$K_{obs} = nK$$

= new const.

Now at initial $t=0$ concentration of 'A' suppose $[A]_0$

and $t=t$ time " " $[A]$

then

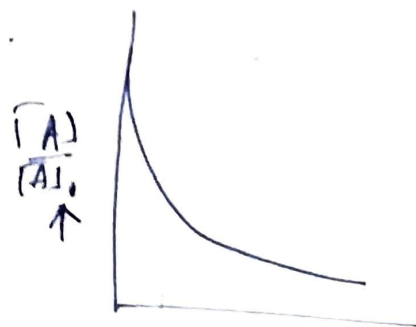
$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = K_{obs} \int_0^t dt$$

$$\ln \frac{[A]}{[A]_0} = -K_{obs} \cdot t$$

$$\text{or } \frac{[A]}{[A]_0} = e^{-K_{obs} \cdot t}$$

$$\text{or } [A] = [A]_0 \cdot e^{-K_{obs} \cdot t}$$

$$\ln \frac{[A]}{[A]_0} = -K_{obs} \cdot t$$



→ t
exponentially decrease.

Now suppose the reaction



Initially
 $t=0$

$$a \qquad 0$$

at $t=t$

$$(a-x) \qquad x$$

$$\text{Rate} = \frac{dx}{dt} = k(a-x)$$

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

$$-\ln(a-x) = kt + C \quad \text{where } C = \text{integration constant.}$$

$$t=0 \quad x=0$$

$$\text{then } -\ln(a-0) = 0 + C$$

$$\therefore C = -\ln a$$

So the reaction become

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

$$\text{or } \ln \frac{a}{a-x} = kt$$

$$\therefore k = \frac{1}{t} \ln \frac{a}{a-x}$$

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

At time when ~~a~~ $x = \frac{a}{2}$, is called
the half life or $t_{1/2}$

$$\therefore t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}}$$

$$= \frac{2.303 \log 2}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

* k has unit = sec^{-1}

for 1st order
reaction.

Q: At 25°C the half-life for the decomposition of N_2O_5 is 5.7 hr. and is independent of the initial pressure of N_2O_5 .
① Calculate the rate constant - ② the time required to go to 90% completion.

$$\Rightarrow t_{1/2} = \frac{0.693}{k}$$
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.7} \text{ hr}^{-1} = 0.1216 \text{ hr}^{-1}$$

Here $k = \frac{1}{t} \ln \frac{a}{a-x}$

When 90% completed $x = 0.9a$

$$0.1216 = \frac{1}{t} \ln \frac{a}{a-0.9a}$$

$$t = \frac{1}{0.1216} \times \ln \frac{a}{0.1a}$$
$$= \frac{2.303}{0.1216} \log 10$$
$$= \frac{2.303}{0.1216} = 18.94 \text{ hr}$$