Illustration 2

The rate law for the reaction

$x + y \longrightarrow z$ is $r = k[x]^{3/2}[y]^{-1/2}$

Find the order and molecularity of reaction.

Soln.: As the above reaction involves two species to form product, thus the molecularity of the reaction is 2.

The order of reaction is $= \frac{3}{2} + \left(-\frac{1}{2}\right) = 1$

ZERO ORDER REACTION

- In a zero order reaction rate is independent of the concentration of reactant.

$$A \longrightarrow \text{product}$$

$t = 0$	a	0
at time t	$(a - x)$	x

$r = k[A]^0 = k[a - x]^0$

On integration, $k = \frac{x}{t}$ or $x = kt$

Unit of rate constant = mol litre^{-1} s^{-1}

- **Half life period :** The period in which concentration becomes half of its initial value, is known as half life period. Denoted as $t_{1/2}$.

$k = x/t$

$t = t_{1/2}$

So $\boxed{t_{1/2} = \frac{a}{2k}}$ a = initial concentration

- **Examples :** Photochemical reactions

$$2NH_3 \xrightarrow{Pt} N_2 + 3H_2$$

FIRST ORDER REACTION

- In first order reaction, the rate is determined by the change of one concentration term only.

For a reaction $A \longrightarrow$ product

$$r = \frac{dx}{dt} = k(a - x) \text{ or } \frac{dx}{(a-x)} = kdt$$

On integration, $\int \frac{dx}{(a-x)} = \int kdt$

i.e. $-\ln(a - x) = kt + c$ where c is integration constant, when $t = 0$, $x = 0$ then $-\ln a = c$

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

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

$$k = \frac{1}{t}\ln\frac{a}{(a-x)} = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

Unit of rate constant = time^{-1}

- **Half life period :**

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

at $t = t_{1/2}$, $\quad x = a/2$

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

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

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

Thus, half life period of first order reaction is independent of initial concentration.

- **Example :**

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

$H_2O_2 \xrightarrow{I^-} 2H_2O + \frac{1}{2}O_2$

n^{th} ORDER REACTION

Half life : $t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)(a)^{n-1}}$

Rate constant $k = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{(a)^{n-1}}\right]$

Illustration 3

The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 is a first order reaction

(i) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.

Soln.:

(i) $2Cl_2O_{7(g)} \rightarrow 2Cl_{2(g)} + 7O_{2(g)}$

For 1st order reaction,

$$k = \frac{2.303}{t}\log\left(\frac{P_0}{P}\right) = \frac{2.303}{55}\log\left(\frac{0.062}{0.044}\right) = 6.2 \times 10^{-3}\ s^{-1}$$

(ii) $k = \frac{2.303}{t}\log\left(\frac{P_0}{P}\right)$

Her e $k = 6.2 \times 10^{-3}$ s^{-1}, $t = 100$ s, $P_0 = 0.062$ atm

$$\therefore \quad 6.2 \times 10^{-3} = \frac{2.303}{100}\log\left(\frac{0.062}{P}\right)$$

$$\text{or } \log\frac{0.062}{P} = \frac{6.2 \times 10^{-3} \times 100}{2.303} \Rightarrow P = 0.033 \text{ atm}$$

Illustration 4

The half life for the reaction, $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + O_{2(g)}$ is 2.4 hr at 30°C. (a) Starting with 10 g, what is the mass of N_2O_5 left after 9.6 hr? (b) How much time is required to reduce 5.0×10^{10} molecules of N_2O_5 to 1.0×10^8 molecules?

Soln.: For a first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.4 \times 60 \times 60} = 8.02 \times 10^{-5}\ s^{-1}$$

(a) Now using the expression

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

$a = 10$ g, $t = 9.6$ hr $= 9.6 \times 60 \times 60$ s; $k = 8.02 \times 10^{-5}$ s^{-1}

$$8.02 \times 10^{-5} = \frac{2.303}{9.6 \times 60 \times 60}\log\frac{10}{a-x}$$