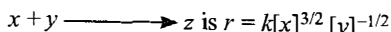


Illustration 2

The rate law for the reaction



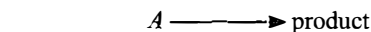
Find the order and molecularity of reaction.

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

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

ZERO ORDER REACTION

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



$$t = 0 \quad a \quad 0$$

$$\text{at time } t \quad (a-x) \quad x$$

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

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

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

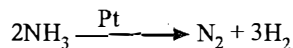
- Half life period :** The period in which concentration becomes half of its initial value, is known as half life period. Denoted as $t_{1/2}$.

$$k = x/t$$

$$t = t_{1/2}$$

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

- Examples :** Photochemical reactions

**FIRST ORDER REACTION**

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

For a reaction $A \longrightarrow \text{product}$

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

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

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

when $t = 0, x = 0$ then $-\ln a = c$

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

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

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

Unit of rate constant = time^{-1}

- Half life period :**

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

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

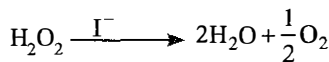
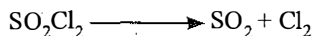
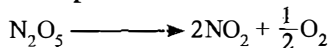
$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{(a-a/2)} = \frac{2.303}{t_{1/2}} \log 2$$

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

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

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

- Example :**

 **n^{th} ORDER REACTION**

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

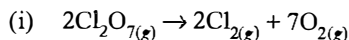
$$\text{Rate constant } k = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{(a)^{n-1}} \right]$$

Illustration 3

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

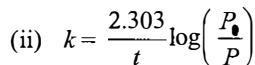
- After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.
- Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.

Soln.:



For 1st order reaction,

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



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

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

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

Illustration 4

The half life for the reaction, $\text{N}_2\text{O}_{5(g)} \rightarrow 2\text{NO}_{2(g)} + \text{O}_{2(g)}$ 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

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

- Now using the expression

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

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

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