

D. B. College (Jaynagar) Lect-28

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Ex. 10

For a reaction $3A \rightarrow \text{Products}$, it is found that the rate of reaction doubles if concentration of A is increased four times, calculate order of reaction.

Sol.ⁿ

Rate = $k[\text{Reactant}]^n$ if $[\text{Reactant}] = a$; rate = r_1

$$r_2 = k[a]^n$$

if $[\text{Reactant}] = 4a$; rate = $2r_1$

$$2r_1 = k[4a]^n$$

$$\therefore \frac{1}{2} = \left[\frac{1}{4}\right]^n \quad \therefore n = \frac{1}{2}$$

Ex. 11

The amount of $^{14}_6\text{C}$ isotope in a piece of wood is found to be one fifth of that present in a fresh piece of wood. Calculate the age of the piece of wood (half-life of $^{14}_6\text{C} = 5577$ years).

Sol.ⁿ Rate of reaction = $\frac{1}{2}$ rate of disappearance of A

$$= \frac{1}{2} \left(-\frac{d[A]}{dt} \right) = \frac{1}{2} \left[\frac{0.5 - 0.4}{10} \right] = 0.005 \text{ mol litre}^{-1} \text{ minute}^{-1}$$

Ex. 13

The time required for 10% completion of the first order reaction at 298 K is equal to that required for its 76% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 \text{ s}^{-1}$, calculate its energy of activation.

Sol.

For first order reactions,

$$t = \frac{2.303}{k} \log \frac{N_0}{N_t}$$

$$\text{At } 298 \text{ K; } t = \frac{2.303}{k_{298}} \log \frac{100}{90}$$

$$\text{At } 308 \text{ K; } t = \frac{2.303}{k_{308}} \log \frac{100}{76}$$

Since time is same

$$\frac{2.303}{k_{298}} \log \frac{100}{90} = \frac{2.303}{k_{308}} \log \frac{100}{76}$$

$$\text{or, } \frac{0.0458}{k_{298}} = \frac{0.1191}{k_{308}}$$

$$\text{or, } \frac{k_{308}}{k_{298}} = \frac{0.1191}{0.0458} = 2.60$$

According to Arrhenius equation,

$$2.303 \log \frac{k_{308}}{k_{298}} = \frac{E_a}{8.314} \left[\frac{1}{298} - \frac{1}{308} \right]$$

$$\text{or } 2.303 \log 2.60 = \frac{E_a}{8.314} \left[\frac{10}{298 \times 308} \right]$$

$$E_a = 72.93 \text{ kJ}$$

Ex. 14 In a reaction, the decrease in reactant's concentration is 20% in 20 minute and 40% in 40 minute. Calculate order of reaction and rate constant.

Solⁿ For a zero order reaction: $t = \frac{x}{k}$ or $k = \frac{x}{t}$
 if $t = t_{20\%} = 20 \text{ minute}$, $x = 20$

$$\text{Then } k = \frac{20}{20} = 1 \text{ mol litre}^{-1} \text{ minute}^{-1}$$

if $t = t_{40\%} = 40 \text{ minute}$, $x = 40$

Then $k = \frac{40}{40} = 1 \text{ mol litre}^{-1} \text{ minute}^{-1}$; Thus, reaction is zero order.

Ex. 15 The rate constant for decomposition of a certain substance is $2.80 \times 10^{-3} \text{ min}^{-1} \text{ s}^{-1}$ at 30°C and $1.38 \times 10^{-2} \text{ min}^{-1} \text{ s}^{-1}$ at 50°C. Evaluate the Arrhenius parameters of the reaction. ($R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$)
 Energy of activation (E_a) and pre-exponential factor A are Arrhenius parameters.

Solⁿ

$$k_1 = 2.80 \times 10^{-3} \text{ min}^{-1} \text{ s}^{-1} \text{ at } 303 \text{ K}$$

$$k_2 = 1.38 \times 10^{-2} \text{ min}^{-1} \text{ s}^{-1} \text{ at } 323 \text{ K}$$

$$\text{As } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$$\therefore E_a = \frac{2.303 R T_1 T_2}{(T_2 - T_1)} \log_{10} \frac{k_2}{k_1}$$

$$E_a = \frac{2.303 \times 8.314 \times 10^{-3} \times 303 \times 323}{(323 - 303)} \log_{10} \left(\frac{1.38 \times 10^{-2}}{2.80 \times 10^{-3}} \right) = 64.91 \text{ kJ mol}^{-1}$$

$$\text{Also, } k = A e^{-E_a/RT}$$

$$\text{or } A = k e^{E_a/RT} = 2.80 \times 10^{-3} e^{64910/8.314 \times 303} = 434 \times 10^3$$