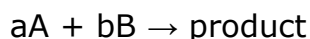


Chemical Kinetics

Q. 1. What is order of a reaction? Derive an expression for a first order reaction. What is half life period?

Ans. Order of a reaction: Number of those reactant molecular species whose conc. actually changes as a result of reaction. Or, it is the sum of the powers to which reactant terms must be raised to express the rate of reaction completely.



Let x moles of A and y moles of B are involved, where conc. changes in rate determining or slowest step.

$$\text{order of reaction} = (x + y), r \propto C_A^x \cdot C_B^y$$

First order reactions : Expression for a first order reaction :



Concentration of reactant at $t = 0$ is "a"

say dx is gain in conc. of product in time dt

conc. of reactant at "t" is $a - x$

Therefore, $\frac{dx}{dt} (a - x)$ or $\frac{dx}{dt} = k(a - x)$ or $\frac{dx}{(a - x)} = k dt$

integrating this reaction $\int \frac{dx}{(a - x)} = \int k dt$

$$-\log(a - x) = kt + C \dots\dots\dots(i) \text{ If } t = 0, x = 0$$

$$\text{So, } -\log a = C \dots\dots\dots(ii)$$

putting value of (ii) in (i)

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

$$\text{or } \log_e \frac{a}{(a - x)} = kt \text{ or } 2.303 \log_{10} \frac{a}{(a - x)} = kt$$

$$k = [2.303/t \cdot \log_{10} a/(a - x)] \dots\dots\dots(iii)$$

Half life period $T_{1/2}$ (Time required to bring half change)

At $T_{1/2} = t$, $x = 0.5a$. putting value in equation (iii)

$$k = 2.303/t_{1/2} \cdot \log_{10} a/(a - 0.5a) = 2.303/T_{1/2} \log_{10} 2$$

$$= (2.303 \times 0.3010)/T_{1/2}$$

$$[k = 0.693/T_{1/2}]$$

Q. 2. The reaction $A + 3B \rightarrow 2C$ obeys the rate equation $\text{Rate} = k [A]^{1/2} [B]^{3/2}$ What is the order of this reaction?

$$\text{Ans Order} = (1/2) + (3/2) = 2$$

Q. 3. A reaction is 50% complete in 2 hrs and 75% complete in 4 hrs. What is the order of reaction?

Ans.

$$t_{1/2} = 2 \text{ hrs}$$

$\therefore$ 75% completion takes in 4 hrs that is two half lives. Hence,

$t_{1/2}$ is independent of initial concentration. It is a first order reaction.

Q. 4. How does change in temperature effects rate constant? Write the relationship, which explains the temperature dependence of a reaction.

Ans. For a chemical reaction, every 10° rise in temperature, nearly doubles the rate constant. Arrhenius established the relationship between rate constant and temperature of reaction.

$$k = Ae^{-E_a/RT}$$

Where, A = Arrhenius factor / frequency factor

E_a = Activation energy in J mol^{-1}

Q. 5. The slope of a line in the graph of $\log_{10} K$ verses $(1/T)$ for a reaction is -5642K . Calculate the activation energy for this reaction.

Ans.

$$\text{Slope} = \frac{E_a}{2.303R}$$

$$\text{Or } E_a = \text{slope} \times 2.303 \times R$$

$$= -(-5642) \times 2.303 \times 8.314$$

$$= 108028.18 \text{ J mol}^{-1}$$

$$= 108.0 \text{ kJ mol}^{-1}$$

Q. 6. Write differences between molecular and order of reaction.

Ans.

Molecularity	Order
1. It is the total number of molecules as present in balanced chemical reaction leading to formation of products.	It is the total number of molecules
2. Molecularity of reaction can never be in fractions.	Order of reaction can be in fractions.
3. Molecularity of reaction cannot be zero.	Order of reaction can be zero.

Q. 7. The rate of a chemical reaction gets doubled after an increase of 10 K in absolute temperature from 298K. Calculate E_a .

Ans.

Let $K_1 = K$

$$K_2 = 2K$$

$$T_1 = 298K$$

$$T_2 = 308K$$

By using

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{2K}{K} = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{10}{298 \times 308} \right]$$

$$E_a = \frac{\log 2 \times 19.147 \text{ J mol}^{-1} \times 298 \times 308}{10}$$

$$= 26.4 \text{ kJ/mol}$$