

Chemical Kinetics

Key Concepts

Rate of chemical reaction- The change in concentration of any reactant or product per unit time is called rate of reaction.

TYPES OF RATE OF REACTION-

1. **Average rate of reaction-** The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \Delta x / \Delta t = -\Delta[R] / \Delta t = +\Delta[P] / \Delta t$$

2. **Instantaneous rate of reaction-** The rate of reaction measured at a particular instant of time is called instantaneous rate of reaction.

$$\text{Instantaneous rate } dx/dt = -d[R]/dt = d[P]/dt$$

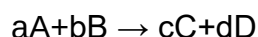
FACTORS AFFECTING RATE OF REACTION-

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation

RATE CONSTANT (k)- It is equal to the rate of reaction when molecular concentration of reactant is at unity.

RATE LAW- The rate of reaction is directly proportional to the product of concentration of reactant and each concentration term is raised to some power which may or may not be equal to stoichiometric coefficient.

For a reaction



$$\text{Rate law} = k[A]^p[B]^q$$

Where powers P and Q are determined experimentally.

MOLECULARITY – The total no. of reactants taking part in elementary chemical reaction is called molecularity.

ORDER OF REACTION- The sum of powers to which the concentration terms are raised in a rate law expression is called order of reactions. For above case order = P+Q: Order of a reaction is determined experimentally.

HALF-LIFE PERIOD- The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

ACTIVATION ENERGY- The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy. OR

Minimum energy required to initiate the chemical reaction.

TEMPERATURE COEFFICIENT- The ratio of rate constant at two temperatures having difference of 10⁰C is called temperature coefficient.

Temperature coefficient = Rate constant at T+10⁰C/Rate constant at T⁰C

Arrhenius Equation-

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

K-rate constant

A-Arrhenius energy

E_a-Activation energy

R- Rate constant

T-Temperature

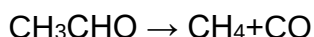
$$\log K = \log A - E_a / (2.303RT)$$

Energy of activation can be evaluated as

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

1 MARK QUESTION

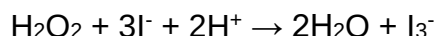
1. The gas phase decomposition of acetaldehyde



Follows the rate law of 3/2 order. What is the unit of its rate constant?

Ans. $\text{mol}^{-1/2} \text{ L}^{1/2} \text{ sec}^{-1}$ [Hint: Unit of rate constant: $(\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$]

2. State the order with respect to each reactant and overall reaction.

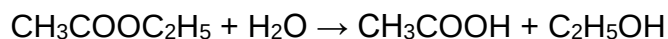


$$\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

Ans. Order of reaction = 1+1 = 2

3. Give one example of pseudo first order reaction.

Ans. Hydrolysis of an ester



4. The conversion of molecules X to Y follows the second order of kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y.

Ans. Rate, $R_1 = k [\text{X}]^2$

After increase, Rate, $R_2 = k [3\text{X}]^2$

$$= 9k [\text{X}]^2 = 9 R_1$$

The rate of formation will become nine times.

5. The rate law for a reaction is

$$\text{Rate} = K [\text{A}] [\text{B}]^{3/2}$$

Can the reaction be an elementary process? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularity and therefore must be in integral form.

6. Why rate of reaction does not remain constant throughout?

Ans: The reaction rate depends on concentration of the reactants. As a reaction proceeds, the concentration of reactants goes on reducing, the rate of reaction goes on reducing.

7. Define specific reaction rate or rate constant.

Ans: The rate of reaction when the concentration of the reacting species is unity.

8. Write the expression for half-life period of zero and first order reaction?

Ans: For zero order $t_{1/2} = R_0 / 2K$

For first order $t_{1/2} = 0.693 / K$

2 MARKS QUESTION

1. The rate of a particular reaction quadruples when the temperature changes from 293K to 313K. Calculate activation energy.

Ans. $\frac{k_2}{k_1} = 4,$

$T_1 = 293K$

$T_2 = 313K$

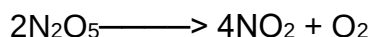
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log [K_2/K_1] = E_a[T_2-T_1]/19.15 \quad [\because 2.303 R = 2.303 \times 8.315 \text{ JK}^{-1} \text{ mol}^{-1} = 19.15 \text{ JK}^{-1} \text{ mol}^{-1}]$$

Thus on calculating and substituting values we get....

$$E_a = 52.86 \text{ kJ mol}^{-1}$$

2. If the decomposition of nitrogen penta oxide as



follows a first order kinetics.

(i) Calculate the rate constant for a 0.05 M solution if the instantaneous rate is $1.5 \times 10^{-6} \text{ mol/l/s}$?

Ans. Rate = K [N₂O₅]

$$K = \frac{\text{Rate}}{[\text{N}_2\text{O}_5]}$$

$$[\text{N}_2\text{O}_5]$$

$$K = \frac{1.5 \times 10^{-6}}{0.05}$$

$$0.05$$

$$K = 3.0 \times 10^{-5}$$

ii) What concentration of N₂O₅ would give a rate of $2.45 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$

$$\text{Rate} = 2.45 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

$$[\text{N}_2\text{O}_5] = \frac{\text{Rate}}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$$

$$K \quad 3.0 \times 10^{-5}$$

$$= 0.82 \text{ M}$$

3) Write the difference between order and molecularity of reaction.

Ans.	ORDER	MOLECULARITY
(1) It is the sum of the powers of concentration terms in the rate law expression.	(1) It is the number of reacting species undergoing simultaneously Collision in a reaction.	
(2) It is determined experimentally	(2) it is a theoretical concept	
(3) It need not to be a whole number	(3) It is whole no. only	
(4) Order of reaction can be zero, fractional.	(4) It can't be zero or fractional	

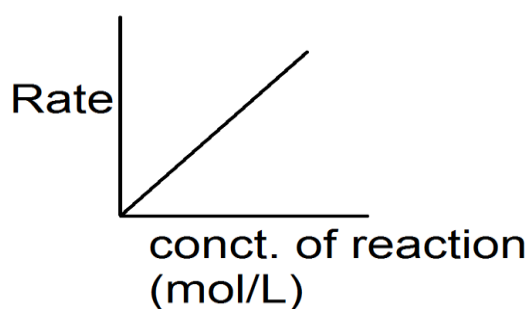
4) Define Threshold energy and activation energy. How they are related?

Ans. Threshold Energy: It is the minimum amount of energy which the reactant molecules must possess for the effective collision in forming the products.

Activation Energy: It is the excess energy required by the reactants to undergo chemical reaction.

Activation energy = Threshold energy – Average kinetic energy of molecules.

5(a). Draw a schematic graph showing how the rate of a first order reaction changes in concentration of reactants.



Variation of rate of first order reaction with concentration.

(b). rate of reaction is given by the equation

$$\text{Rate} = k [A]^2 [B]$$

What are the units of rate constant for this reaction?

Ans. Rate = $k [A]^2 [B]$

$$K = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^2 (\text{mol L}^{-1})}$$

$$K = \text{mol}^{-2} \text{L}^2 \text{s}^{-1}$$

$$K = \text{mol}^{-2} \text{L}^2 \text{s}^{-1}$$

3 marks question

Q1. The rate constant for first order reaction is 60 per s. How much time will it take to reduce the concentration of the reactant to 1/10 of its initial value.

Ans:-

$$t = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{K} \log \frac{[R_0]}{[R_0] \times 0.1}$$

$$t = \frac{2.303}{60} \log 10$$
$$t = \frac{2.303}{60} = 3.38 \times 10^{-2} \text{ s}^{-1}$$

2. The rate of most of reaction double when their temperature is raised from 298k to 308k. Calculate the activation energy of such a reaction.

Ans:-

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89 \text{ KJ/mol}$$

3. A first order reaction takes 69.3 min for 50% completion. Set up an equation for determining the time needed for 80% completion.

Ans. $K = \frac{0.693}{t_{1/2}}$

$$= 0.693/69.3 \text{ min}$$

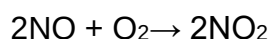
$$= 10^{-2} \text{ min}^{-1}$$

$$T = \frac{2.303}{K} \log \frac{[R_0]}{[R]} = \frac{2.303}{K} \log \frac{[100]}{20}$$

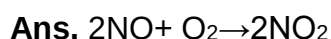
$$T = 2.303/10^{-2} \log 5$$

$$T = 160.9 \text{ min}$$

4. Following reaction takes place in one step



How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume? Will there be any change in the order of reaction with reduced volume?



$$dx/dt = k \times [\text{NO}]^2 [\text{O}_2]^1$$

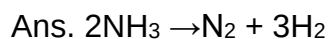
[Since it is one step]

If the volume of reaction vessel is diminished to 1/3, conc. Of both NO and O₂ will become 3 times, the rate of reaction increased 27 times.

In the order of reaction with the reduced volume.

5. The decomposition of NH₃ on platinum surface is a zero order reaction. What are the rate of production of N₂ and H₂.

If $k = 2.5 \times 10^{-4}$



$$\frac{-1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} + \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\frac{-d[\text{NH}_3]}{dt} = \text{rate} = k \times [\text{NH}_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\frac{d[\text{N}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$= 1/2 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\begin{aligned} d[\text{H}_2] &= - \frac{3}{2} \frac{d[\text{NH}_3]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4} \\ &= 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate} &= - \frac{d[\text{NH}_3]}{dt} = k [\text{NH}_3]^0 \\ &= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1} \\ \text{Rate of production of N}_2 &= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1} \end{aligned}$$