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UNIT-4

CHEMICAL KINETICS

CONCEPT

Thermodynamics helps us to predict the feasibility of chemical reaction by using ΔG as parameter but it cannot tell everything about the rate of reaction. Rate of chemical reaction is studied in another branch of chemistry called Chemical Kinetics.

Chemical kinetics- The branch of physical chemistry which deals with the study of rate of reaction and their mechanism is called chemical kinetics.

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 time is called instantaneous rate of reaction.

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

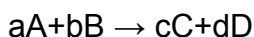
FACTORS AFFECTING RATE OF REACTION-

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 is raised to some power which may or may not be equal to stereochemistry experimentally.

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 concentrations terms are raised in a rate law expression is called order of reactions. For above case order = P+Q: orders of r^n 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.

$$\text{Activation energy} = \text{Threshold energy} - \text{kinetic energy}$$

TEMPERATURE COEFFICIENT- The ratio of rate constant at two temperatures having difference of 10^0C is called temperature coefficient.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } T+10^0\text{C}}{\text{Rate constant at } T^0\text{C}}$$

Arrhenius Equation-

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

K-rate constant

A-Arrhenius energy

E_a-Activation energy

R- Rate constant

T-Temperature

$$\log K = \log A - \frac{E_a}{2.303RT}$$

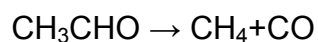
Energy of activation can be evaluated as

$$1. \log [K_2/K_1] = \frac{E_a(1/T_1 - 1/T_2)}{2.303RT}$$

$$\log [K_2/K_1] = \frac{E_a(1/T_1 - 1/T_2)}{19.15}$$

1 MARKS QUESTION

1. The gas phase decomposition of acetaldehyde

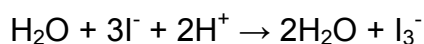


Follows the rate law.

What are the units of its rate constant.

Ans. $\text{Atm}^{-1/2}\text{sec}^{-1}$

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

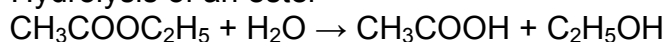


$$\text{Rate} = k[\text{H}_2\text{O}_2]^1[\text{I}^-]^1$$

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.

$$\begin{aligned}\text{Ans. Rate} &= k [\text{A}]^2 \\ &= k [3\text{A}]^2 \\ &= k [9\text{a}]^2\end{aligned}$$

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 molecularities and therefore must be in integral form.

6. What do you understand by 'rate of reaction'?
7. Name the factors on which the rate of a particular reaction depends.
8. Why rate of reaction does not remain constant throughout?
9. Define specific reaction rate or rate constant.

10. What is half-life period of a reaction?

2 MARKS QUESTION

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

Ans. $K_2/K_1 = 4$,

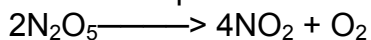
$$T_1 = 293K \quad T_2 = 313K$$

$$\log [K_2/K_1] = E_a [T_2 - T_1] / 19.15$$

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

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

2. If the decomposition of nitrogen 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 = $K [\text{N}_2\text{O}_5]$

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

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

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

ii) What concentration of N_2O_5 would give a rate of $2.45 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$

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

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

$$= 0.82 \text{ M}$$

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

Ans. ORDER

MOLECULARITY

It is the sum of the powers of concentration terms in the rate law expression.

It is the number of reacting species undergoing simultaneously Collision in a reaction.

It is determined experimentally

it is a theoretical concept

Order of reaction need not be a whole number

It is whole no. only

Order of reaction can be zero.

It can't be zero or fractional

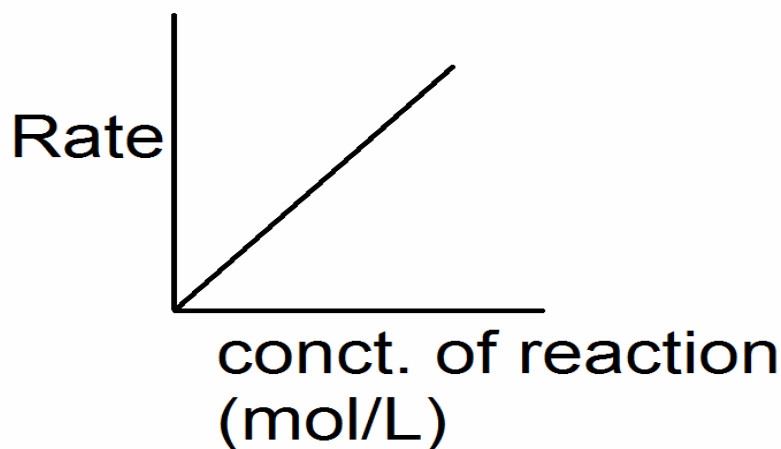
4) Define Threshold energy and activation energy. How they are related?

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 of first order reaction with concentration.

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

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

What are the units of rate constant for this reaction?

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

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

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

6. List the factors affecting the rate of reaction.

7. Explain with suitable example, how the molecularity of a reaction is different from the order of a reaction.

8. Define the term 'rate constant' of 'specific reaction rate'.
 9. What are Pseudo unimolecular reactions? Explain with the help of a suitable example.
 10. What is half life period? Derive an expression for half-life period in case of a first order reaction.

3 marks question

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

Ans:-

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

$$t = \frac{2.303}{60} \log \frac{[R_0]}{\frac{1}{10} [R]}$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60} = 3.84 \times 10^{-2} \text{ s}^{-1}$$

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:-

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

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

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

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. $K = \frac{0.693}{T^{1/2}}$

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

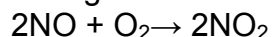
$$= 10^{-2} \text{ min}^{-1}$$

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

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

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

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?

Ans. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

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

[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 time, 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 $k = 2.5 \times 10^{-4}$

Ans. $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$

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

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

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

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

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

$$d[\text{H}_2] = -\frac{3}{2} \frac{d[\text{NH}_3]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

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

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

$$\text{Rate of production of N}_2 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

6. How is the rapid change in concentration of reactants/products monitored for fast reactions.

7. What are photochemical reactions? Give two examples,

8. What is the effect of temperature on the rate of reaction? Explain giving reasons.

9. Comment on free energy change of 'photochemical reactions'.

10. State the role of activated complex in a reaction and state its relation with activation energy.

QUESTIONS CARRYING 5 MARKS

1. What do you understand by the rate of a reaction? How it is expressed? How it is the rate of reaction determined?
2. What do you understand by order of a reaction? How does rate law differ from law of mass action? Give two example of each of the reactions of (i) zero order (ii) first order (iii) second order
3. Derive the equation for the rate constant for a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in mole per litre and time in seconds.
4. Explain why the rate of reaction increases with increase in temperature.
5. Briefly explain the effect of temperature on the rate constant of a reaction.

HOTS

1. The half-life period of two samples are 0.1 and 0.4 seconds. Their initial Concentrations are 200 and 50 mol L⁻¹ respectively. What is the order of reaction?
2. What is the ratio of $t_{3/4} : t_{1/2}$ for a first order reaction ?
3. Higher molecularity reactions (viz. molecularity, 4 and above) are very rare. Why?
4. Consider the reaction $2A + B \longrightarrow \text{Products}$

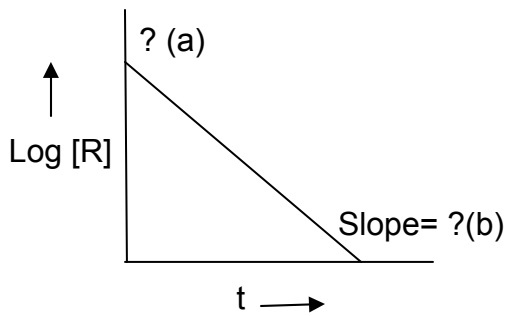
When concentration of B alone was doubled, half life time does not change. When conc. of A alone is doubled, the rate increases by two times. What is the unit of K and what is the order of the reaction?

5. For the reaction, the energy of activation is 75KJ / mol. When the energy of activation of a catalyst is lowered to 20KJ / mol. What is the effect of catalyst on the rate of reaction at 20°C.

6. The gas phase decomposition of CH_3OCH_3 follows first order of kinetics
 $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4(\text{g}) + \text{H}_2(\text{g}) + \text{CO}(\text{g})$
 The reaction is carried out at a constant volume of the container at 500°C and has $t_{1/2} = 14.5\text{min}$.
 Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal behavior.
- Q 7. See the graph and answer the following question

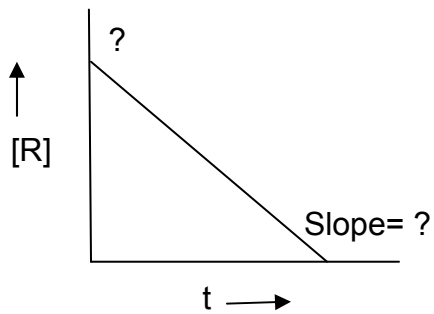
- 1). What is the order of r^n

2) what is the value of a and b

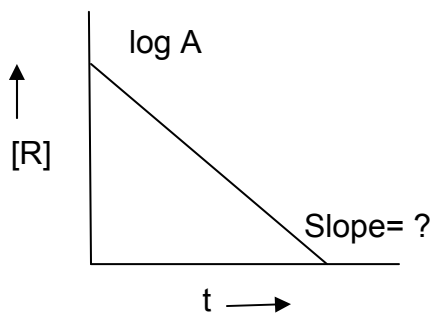


q 8. 1) what is the order of r^n

2) what is the value of slope and intercept



q 9.1). what is the value of slope



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