Chapter - 4

CHEMICAL KINETICS

1 MARKS QUESTION

1. The gas phase decomposition of acetaldehyde
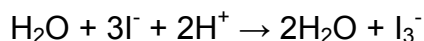
$$CH_3CHO \rightarrow CH_4 + CO$$
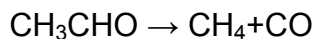
Follows the rate law.

What are the units of its rate constant.

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

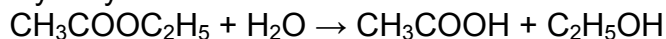**2.** State the order with respect to each reactant and overall reaction.

$$H_2O + 3I^- + 2H^+ \rightarrow 2H_2O + I_3^-$$

Rate = $k[H_2O_2]^1[I^-]^1$

Ans. Order of reaction= 1+1= 2

3. Give one example of pseudo first order reaction.

Ans. Hydrolysis of an ester
$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

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 = $k[A]^2$
$$= k[3A]^2$$
$$= k[9a]^2$$

The rate of formation will become nine times.

5. The rate law for a reaction is
Rate = $K[A][B]^{3/2}$
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.
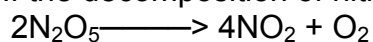
Ans. $K_2/K_1 = 4$,

  T1= 293K T2 = 313K

  Log [K2/K1] = Ea[T2-T1]/19.15

  Thus on calculating and substituting values we get…..

  Ea = 52.86 KJ mol^{-1}

2. If the decomposition of nitrogen oxide as
  $2N_2O_5 \longrightarrow 4NO_2 + O_2$
  follows a first order kinetics.
(i) Calculate the rate constant for a 0.05 M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s?

Ans. Rate = K $[N_2O_5]$

  K= $\dfrac{Rate}{[N_2O_5]}$

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

K= 3.0×10^{-5}

ii) What concentration of N_2O_6 would give a rate of 2.45×10^{-5} mol $L^{-1}s^{-1}$
  Rate = 2.45×10^{-5} mol $L^{-1}s^{-1}$
  $[N_2O_5]$ = $\dfrac{Rate}{K}$ = $\dfrac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$
    = 0.82 M

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

| ORDER	MOLECULARITY
It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting speci--es 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.
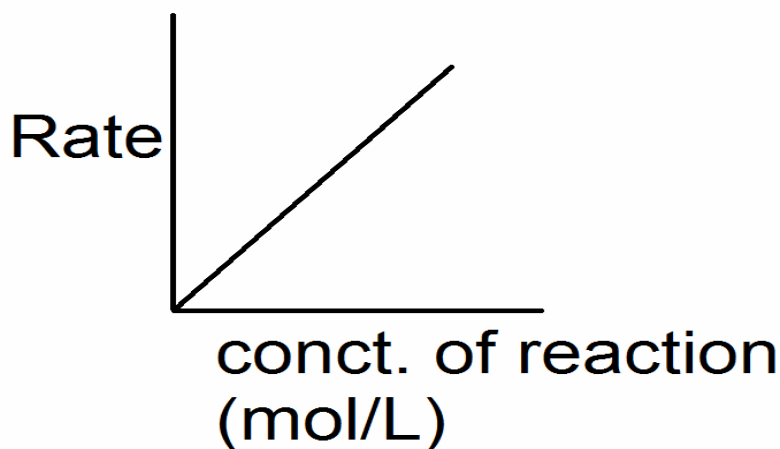
Variation of rate of first of first order reaction with concentration.

(b). rate of reaction is given by the equation
        Rate = k [A] 2[B]
        What are the units of rate constant for this reaction?
Ans. Rate = k [A] 2[B]

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

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 and 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:-

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

$$t = \frac{2.303}{\frac{1}{10}} \log \frac{[R0]}{[R]}$$

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

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

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:-

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 \, R} \frac{1 - 1}{T_1 \, T_2}$$

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

$$E_a = 52.89 KJ/mol$$

3. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion.
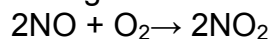
Ans. $K = \frac{0.693}{T^{1/2}}$

$= 0.693/69.3 min$

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

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

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

$T = 160.9 min$

4. Following reaction takes place in one step

$$2NO + O_2 \rightarrow 2NO_2$$

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. $2NO + O_2 \rightarrow 2NO_2$

$dx/dt = k*[NO]_2[O_2]1$

[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 NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2.
If k= 2.5×10^{-4}

Ans. $2NH_3 \rightarrow N_2 + 3H_2$

$$\frac{-1}{2}\frac{d[NH_3]}{dt} = \frac{d[NH_2]}{dt} + \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{-d[NH_3]}{dt} = rate = k \times [NH_3]^0$$

$$= 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$= 1/2 \times 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = 3/2 \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-44}molL^{-1}sec^{-1}$$

$$Rate = -\frac{d[NH3]}{dt} = k \times [NH3]^0$$

$$= 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$$

Rate of production of N_2 = $2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$

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.

IMPORTANT QUESTIONS

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 _____> 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 20^0C.

6. The gas phase decomposition of CH_3OCH_3 follows first order of kinetics
$CH_3OCH_3 \rightarrow CH_4 (g) + H_2 (g) + CO (g)$
The reaction is carried out at a constant volume of the container at 500^0 C and has $t_{1/2}$ =14.5min.
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.
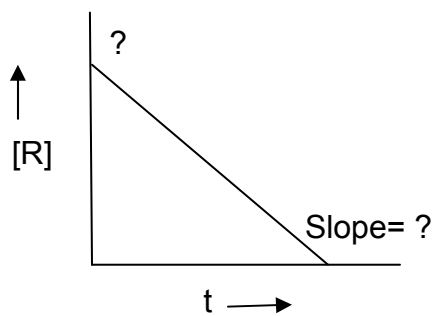Q 7. See the graph and answer the following question

1). What is the order of r^n

2) what is the value of a and b

? (a)

Log [R]

Slope= ?(b)

t ⟶
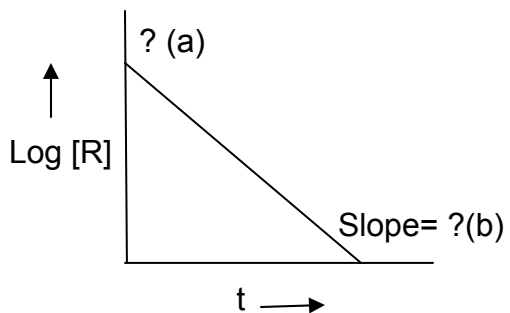
q 8. 1) what is the order of r^n
2) what is the value of slope and intercept

?

[R]

Slope= ?

t ⟶

q 9.1). what is the value of slope

log A

[R]

Slope= ?

t ⟶