Chapter -4

Chemical kinetics

Theory problems

1. What is the difference between order of the reaction and molecularity of the reaction.
2. Write the unit of rate constant for-
   a. Zero order reaction
   b. First order reaction
   c. Second order reaction
3. Consider the following graph and answer the given question-
   a. What is order of reaction?
   b. What is rate law for this reaction
   c. What the unit is of rate const.
   d. How much time the rate will change if concentration is reduced by factor 2.

4. Reaction $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ takes place in following two step-

   $2NO + H_2 \rightarrow N_2 + H_2O_2$ slow

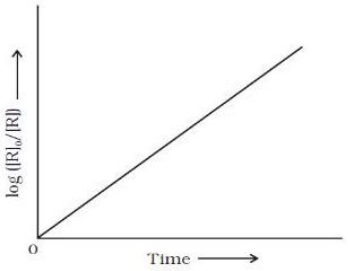
   $H_2O_2 + H_2 \rightarrow 2H_2O$ fast

   Now answer the following question-

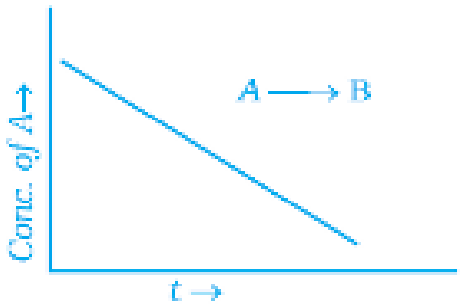
   a. Write the rate law for this reaction
   b. What is order of the reaction?
   c. What is the molecularity of the reaction at each individual step
   d. What is the unit of rate const if concentration is expressed in mol dm^{-3} and time in hours
5. For the reaction-

   $$C_{12} + H_{22} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

   Write-
   a. Rate of reacton expression
   b. Rate law equation
   c. Molecularity
   d. Order of reaction
6. Consider the graph and answer the following question-
   a. What is order of the reaction
   b. What is unit of rate const
   c. What does the slope indicate?
   d. What happens if concentration doubled.



7. For which type of reactions, order and molecularity have the same value?
8. For a general reaction A → B, plot of concentration of A vs time is given in figure. Answer the following question on the basis of this graph-
    a. What is the order of the reaction?
    b. What is the slope of the curve?
    c. What are the units of rate constant?



9. Account the following-
    a. The reaction between H_2 and O_2 is highly feasible yet allowing the gases stand at room temperature in the same vessel does not lead to the formation of water.
    b. Rate of a reaction increase with rise in temperature.
    c. Oxygen is available in plenty in air yet fuels do not burn by themselves at temperature.
    d. The probability of reaction with molecularity higher than three is very rare.
    e. The rate of any reaction generally decreases during the course of the reaction.
    f. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction.
    g. The redox titration of $KMnO_4$ vs oxalic acid, we heat oxalic acid solution before starting the titration?
    h. Molecularity of any reaction can not be equal to zero?
    i. Molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions.
    j. We can't determine the order of a reaction by taking into consideration the balanced chemical equation?
    k. For a reaction A + B → Products, the rate law is — Rate = k $[A][B]^{3/2}$ Can the reaction be an elementary reaction? Explain.
    l. For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow.
    m. For a zero order reaction will the molecularity be equal to zero.

Numerical problems

1. For the reaction R →P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction.
2. Calculate the overall order of a reaction which have rate = k $[A]^{1/2}$ $[B]^{3/2}$
3. Find reaction order if rate constants k = 2.3×10^{-5} L mol^{-1} s^{-1}
4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y
5. In a reaction if the concentration of reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?
6. The initial concentration of N_2O5 in the following first order reaction $N_2O_5 \rightarrow 2\ NO_2 + 1/2O_2$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

7. A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half-life of the reaction.
8. A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?
9. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.
10. The rate constants of a reaction at 500K and 700K are $0.02s^{-1}$ and $0.07s^{-1}$ respectively. Calculate the values of E_a and A.
11. The first order rate constant for the decomposition of ethyl iodide by the reaction at 600K is $1.60 \times 10^{-5}\ s^{-1}$. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

$$C_2H_5I \rightarrow C_2H_4 + HI$$

12. For the reaction:
    $2A + B \rightarrow A_2B$ the rate $= k[A][B]^2$ with $k = 2.0 \times 10^{-6}\ mol^{-2}\ L^2\ s^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1\ mol\ L^{-1}$, $[B] = 0.2\ mol\ L^{-1}$. 4.3
13. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}\ mol^{-1}\ L\ s^{-1}$?
14. A reaction is first order in A and second order in B.
    a. Write the differential rate equation.
    b. How is the rate affected on increasing the concentration of B three times?
    c. How is the rate affected when the concentrations of both A and B are doubled?
15. In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

A/mol L^{-1}	0.20	0.20	0.40
B/mol L^{-1}	0.30	0.10	0.05
r_0/mol $L^{-1}s^{-1}$	5.07×10^5	5.07×10^{-5}	1.43×10^{-4}

    a. Determine the rate law.
    b. Determine rate const.
    c. What is the order of the reaction with respect to A and B?

16. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.
17. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.
18. Consider a certain reaction A → Products with $k = 2.0 \times 10^{-2}s^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is $1.0\ mol\ L^{-1}$.
19. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.00$ hours. What fraction of sample of sucrose remains after 8 hours
20. The decomposition of hydrocarbon follows the equation $k = (4.5 \times 10^{11}s^{-1})\ e^{-28000K/T}$ Calculate E_a.
21. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?