Unit - 4

CHEMICAL KINETICS

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Define the term 'rate of reaction'.
2. Mention the units of rate of reaction.
3. Express the rate of reaction in terms of Br^- (*aq*) as reactant and Br_2 (*aq*) as product for the reaction :

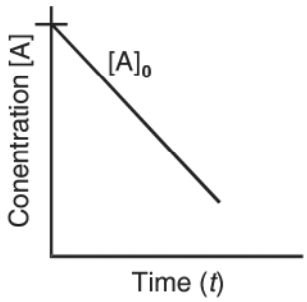
   $5\ Br^-(aq) + Br(aq) + 6H^+\ (aq) \rightarrow 3\ Br_2(aq) + 3H_2O(l)$
4. For a chemical reaction represented by R $\rightarrow$ P the rate of reaction is denoted by

   $$\frac{-\Delta[R]}{\Delta t} \text{ or } \frac{+\Delta[P]}{\Delta t}$$

   Why a positive sign (+) is placed before $\frac{\Delta[P]}{\Delta t}$ and negative sign (–) before $\frac{\Delta[R]}{\Delta t}$?
5. Express the rate of reaction in terms of disappearance of hydrogen and appearance of ammonia in the given reaction.

   $N_2(g) + 3\ H_2\ (g) \rightarrow 2NH_3\ (g)$
6. Why rate of reaction does not remain constant throughout?
7. Write the unit of first order rate constant of a gaseous reaction if the partial pressure of gaseous reactant is given in bar.
8. For a zero order reaction :

   R $\rightarrow$ P, the change in concentration of reactant w.r.t. time is shown by following graph.



9. What will be the order of reaction, if the rate of reaction does not depend on the concentration of any of the reactant.

10. For the elementary step of a chemical reaction :

$H_2 + I_2 \rightarrow 2HI$

rate of reaction α $[H_2]$ $[I_2]$

What is the (i) molecularity and (ii) order of the reaction.

[**Ans. :** (i) 2 (ii) 1]

11. For a chemical reaction A B. The rate of the reaction is given as Rate = k $[A]^n$, the rate of the above reaction quadruples when the concentration of A is doubled. What is the value of n? [**Ans. :** n = 2]

12 Mention one example of zero order reaction.

13. What is the value of the order of reaction of radioactive decay?

[**Ans. :** First order]

*14. Express the relation between the half life period of a reactant and initial concentration for a reaction of n^{th} order.

[Ans : $t_{½} \alpha \frac{1}{[A]_0^{n-1}}$

*15. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction? **Ans :** [First order]

16. Suggest an appropriate reason for the observation : "On increasing temperature of the reacting system by 10 degrees, the rate of reaction almost doubles or even sometimes becomes five folds."

*17. For a chemical reaction, activation energy is zero and at 300K rate constant is 5.9×10^{-5} s^{-1}, what will be the rate constant at 400K?

[**Ans. :** 5.9×10^{-5} s^{-1}]

*18. Two reactions occuring at the same temperature have identical values of Ea. Does this ensure that also they will have the same rate constant? Explain.

[**Hint :** Rate depends on the nature and concentrations of reactants and also pre-exponential factor.

19. The rate constant of a reaction is given by the expression $k = Ae^{-Ea/RT}$ Which factor in this expression should register a decrease so that the reaction proceeds rapidly?

20. For a chemical reaction rate constant $k = 5.3 \times 10^{-4}$ mol L^{-1} s^{-1}, what will be the order of reaction? [**Ans. :** zero order]

21. Write the rate law and order for the following reaction :

$AB_2 + C_2 \rightarrow AB_2C + C$ (slow)

$AB2 + C \rightarrow AB_2C$ (Fast)]

[**Ans. :** Rate = $k [AB_2] [C_2]$; Order = 1 + 1 = 2]

SA (I) TYPE QUESTIONS (2 - MARKS QUESTIONS)

22. List four factors which affect the rate of a chemical reaction. State how each of these factors changes the reaction rate.

23. Differentiate between

(a) Average rate and instantaneous rate of a chemical reaction.

(b) Rate of a reaction and specific rate of reaction, i.e., rate constant.

24. The rate law for the reaction : $A + B \rightarrow P$ is given by

$Rate = k [A]^n [B]^m$

On doubling the concentration of A and reducing the concentration of B to half of its original concentration, calculate the ratio of the new rate to the previous rate of reaction. [**Ans. :** 2^{n-m}]

$$\left[\textbf{Hint :} \frac{\text{New rate}}{\text{Previous rate}} = \frac{k[2A]^n\left[\frac{B}{2}\right]^m}{k[A]^n[B]^m}\right]$$

25. For the reaction in a closed vessel :

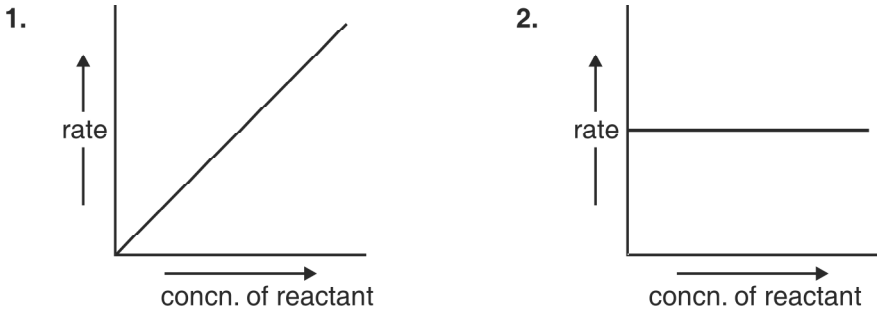
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; $Rate = k [NO]^2 [O_2]$

If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction? [**Ans. :** Diminish to 1/8 of initial value]

26. Explain with an example, what is a pseudo first order reaction?

27. Show that time required for 99.9% completion of the first order reaction is 10 times of $t_{1/2}$ for first order chemical reaction.

28. The graphs (1 and 2) given below are plots of rate of reaction verses concentration of the reaction. Predict the order from the graphs.



29. (a) For a reaction A + B Products, the rate law is given by

$$r = k\,[A]^{1/2}\,[B]^{2}$$

What is the order of reaction?

(b) 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? [**Ans. :** (a) 5/2; (b) 9 times]

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

31. What is meant by zero order reaction? Derive an integrated rate equation for a zero order reaction.

32. (a) Write two points of difference between order of reaction and molecularity of a reaction.

(b) Write one point of difference between rate of reaction and rate constant.

33. Draw a graph between fraction of molecules and kinetic energy of the reacting species for two different temperatures :

(a) Room temperature

(b) Temperature 10°C higher than the room temperature

(c) Indicate the fraction of additional molecules which react at (t +10)°C.

LONG ANSWER TYPE QUESTIONS (5 - MARK - QUESTIONS)

34. (a) A chemical reaction is of second order w.r.t. a reactant. How will the rate of reaction be affected if the concentration of this reactant is : (a) doubled; (b) reduced to 1/8th.

[**Ans. :** (a) Four times (b) 1/64]

(b) For the reaction

$2NO\ (g) + Cl_2\ (g) \rightarrow 2\ NOCl\ (g)$

the following data were collected. All the measurements were taken at 263k

Experiment No.	*Initial [NO] / M*	*Initial [Cl_2] /M*	*Initial rate of disapperance of Cl_2 [M / min]*
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(i) Write the expression for rate law.

(ii) Calculate the value of rate constant and specify its units.

(iii) What is the initial rate of disapperance of Cl_2 in exp. 4?

[**Ans.:** (i) Rate = $k\ [NO]^2\ [Cl_2]$, (ii) $k = 177.7\ L^2\ mol^{-2}\ min^{-1}$, (iii) 2.7765 M/min

35. (a) Draw a plot between log k and reciprocal of absolute temperature (T).

(b) The energy of activation for a chemical reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on the rate of reaction at 20°C, if other factors are equal?

36. (a) Derive the equation for rate constant of a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in moles per litre and time in seconds?

(b) For first order chemical reaction half life period ($t_{1/2}$) is concentration independent. Justify the statement by using integrated rate equation.

NUMERICALS

37. The reaction $SO_2Cl_2(g) \xrightarrow{k} SO_2(g) + Cl_2(g)$ is a first order reaction with half life of 3.15×10^4 s at 575 K. What percentage of SO_2Cl_2 would be decomposed on heating at 575K for 90 min. [**Ans. :** 11.2%]

38. A certain reaction is 50% complete in 20 min at 300K and the same reaction is again 50% complete in 5 min at 350K. Calculate the activation energy if it is a first order reaction.

    (R = 8.314J K^{-1} mol^{-1}, log 4 = 0.602) [**Ans. :** 24.206 kJ/mol]

39. For a chemical reaction A → B, it was found that concentration of B increases by 0.2 mol L^{-1} in half an hour. What is the average rate of reaction.

    [**Ans. :** 0.0066 mol L^{-1} min^{-1}]

40. In the reaction R → P, the concentration of R decreases from 0.03M to 0.02 M in 25 minutes. Calculate the average rate of reaction using unit of time both in minutes and seconds.

    [**Ans. :** 4×10^{-4}M min^{-1}, 6.66×10^{-6} M s^{-1}]

41. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5g of this reactant take to reduce to 3g? [**Ans. :** t = 444 s]

42. The rate of reaction triples when the temperature changes from 20°C to 50°C. Calculate the energy of activation. [R = 8.314 J K^{-1} mol^{-1}, log 3 = 0.48] [**Ans. :** 12.59 kJ]

43. A hydrogenation reaction is carried out at 550 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol–1.

    [**Hint :** $k = Ae^{-E_a/RT}$. In the absence of catalyst, E_a = x kJ mol^{-1}. In the presence of catalyst, E_a = (x – 20) kJ mol^{-1}] [**Ans. :** E_a = 100 kJ mol^{-1}]

44. The rate constant for the first order decomposition of H_2O_2 is given by the following equation log k = 14.34 – 1.25×10^4 K/T. Calculate E_a for this reaction and at what temperature will its half-life be 256 minutes.

    [**Ans. :** E_a = 239.34 kJ; T = 670K]

45. Show that for a first order reaction, time required for 99% completion is twice for the time required for the 90% completion of reaction.

46. The experimental data for the reaction : $2A + B_2 \rightarrow 2AB$, are as follows. Write probable rate expression.

[A] mol/L^{-1}	*[B_2] mol/L^{-1}*	*Initial rate (mol L^{-1} sec^{-1})*
0.5	0.5	1.6×10^{-4}
0.5	1.0	3.2×10^{-4}
1.0	1.0	3.2×10^{-4}

[**Ans :** Rate = k [B_2]

47. A reaction is 20% complete in 20 minutes. Calculate the time required for 80% completion of reaction, If reaction follows the first order kinetics.

[**Ans. :** 144 min]

48. The decomposition of phosphine 4PH3(g) P4(g) + 6H2(g) has rate law; Rate = k [PH_3]. The rate constant is 6.0×10^{-4} s^{-1} at 300K and activation energy is 3.05×10^5 J mol^{-1}. Calculate the value of the rate constant at 310K. (R = 8.314 J K^{-1} mol^{-1}). [**Ans. :** 30.97×10^{-3} s^{-1}]

49. For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data is obtained.

t (sec.)	0	360	720
Pressure (atm.)	35.0	54.0	63.0

Calculate the rate constant.

[**Ans. :** $k_{360} = 2.17 \times 10^{-3}$ s^{-1} ; $k_{720} = 2.24 \times 10^{-3}$ s^{-1}]

50. The decomposition of hydrocarbon follows the equation

$k = (4.5 \times 10^{11}\ s^{-1})\ e^{-28000\ K/T}$,

Calculate activation energy (Ea). [**Ans. :** 232.79 kJmol^{-1})