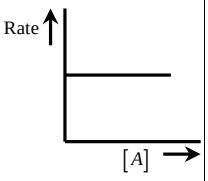
UNIT-4: CHEMICAL KINETICS

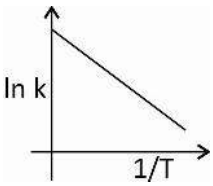
One mark questions:	
1. Differentiate between average and instantaneous rate of a reaction.	U
2. Express the rate of the reaction in terms of different reactants and products for; $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$	U
3. Define order of a reaction.	K
4. What is an elementary reaction?	K
5. Define molecularity of reaction.	K
6. What is the slowest step in a complex reaction also called?	K
7. For what type of reactions is molecularity and order the same?	U
8. What is the order of the reaction for which the rate law is; Rate $= k[A]^{1/2}[B]^{3/2}$	S
9. Unit of rate constant of a reaction is same as the unit of rate of reaction. What is the order of the reaction?	U
10. Mention any one condition under which a second order reaction of rate law: rate = $k[A]^1[B]^1$ can be made a pseudo first order reaction.	U
11. For a reaction, the graph of rate of the reaction against molar concentration of the reactant is as shown. What is the order of the reaction? 	A
12. Rate law of a reaction is : rate = k $[NO]^2$ $[O_2]$. By how many times does the rate of the reaction increase if the volume of the reaction vessel is halved?	S
13. By how many times does the $t_{½}$ of zero order reaction increase if the initial concentration of the reactant is doubled.	S
14. $t_{½}$ of a reaction is 10 minutes, for a first order reaction. What percent of the reactant remains unreacted at the end of 50 minutes? [A:3.125%]	S
15. If $t_{½}$ for a first order reaction is 25 s, what is the time required for 10 g of a reactant to get reduced to 1.25 g? [A: 75 s]	S
16. Oxygen is available in air, yet fuels do not burn spontaneously at room temperature. Why?	A
17. In the Arrhenius equation $k = Ae^{-Ea/RT}$, What does $e^{-Ea/RT}$ represent?	K
18. What is the relationship between the rate constant and activation energy of a reaction?	K
19. Differentiate between activation energy and threshold energy of a reaction.	U

20. For many reactions, it is found that a large number of colliding molecules have energy more than threshold value, yet the rate of the reaction is slow. What might be the reason?	U
21. What is collision frequency?	K
Two mark questions	
1. Mention the factors which affect the rate of a reaction.	U
2. In a reaction 2A $\longrightarrow$ products, the concentration of A decreases from 0.5 to 0.4 mol L^{-1} in 10 minutes. Calculate the rate of reaction during this interval. [A: 5×10^{-3} $Mmin^{-1}$]	S
3. Identify the order of the reaction from the unit of rate constants. i) L mol^{-1} s^{-1} ii) M^{-2} min^{-1}	U
4. Write the order of the reaction and unit of the rate constant for the reaction: $CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$. Rate = k $[CH_3CHO]^{3/2}$	U
5. 2A $\longrightarrow$ P; is second order reaction. How is the rate of the reaction affected if the concentration of A is (a) doubled (b) reduced to half?	S
6. Define half-life period of a reaction. Give an expression for $t_{½}$ for a zero order reaction.	K
7. Show that half-life period for a zero order reaction R $\longrightarrow$ P, is directly proportional to initial concentration of the reactant.	K
8. Show that the half-life period of a first order reaction R $\longrightarrow$ P is independent of initial concentration of the reactant.	K
9. For a zero order reaction: $2NH_{3(g)} \xrightarrow[\Delta]{Pt} N_{2(g)} + 3H_{2(g)}$, the rate constant k = 2 $\times$ 10^{-4} mol L^{-1} s^{-1}. What are the rates of production of N_2 and H_2?	S
10. Time required to decompose SO_2Cl_2 to half of its initial amount in 55 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.	S
11. What happens to half life time of a first order reaction when temperature is increased? Give reason.	A
12. Draw a graph of concentration of R versus time for a zero order reaction R $\longrightarrow$ P. What is the intercept of the line equal to?	S
13. The decomposition of a hydrocarbon follows the equation: k = 4.5×10^{11} $e^{-28000/T}$. Calculate E_a. Given R = 8.314 J K^{-1} mol^{-1}. [A: 232.79 kJ]	S

14. The activation energy for a reaction at the temperature T was found to be 2.303RT J mol^{-1}. Calculate the ratio of the rate constant to Arrhenius factor. [A: 1.25×10^{-2}] S

15. Draw the plot of the distribution curves showing the temperature dependence on the rate of the reaction at two temperatures t and (t+10). Mark E_a and shade the relevant regions to show that fraction of molecules having energy greater than E_a doubles when temperature is increased by 10°. S

16. In the graph, what is the intercept and slope of the line equal to?



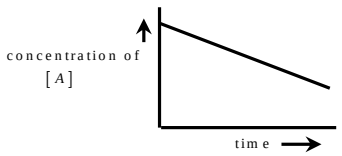
S

17. What does P and Z_{AB} represent in the equation : rate = P Z_{AB} $e^{-Ea/RT}$? K

Three mark questions

1. A reaction is first order in X and second order in Y:
   i) Write the differential rate law of the reaction.
   ii) How is the rate affected on increasing the concentration of Y three times?
   iii) Write the SI unit for the rate constant. S

2. For a general reaction $A \rightarrow B$, plot of concentration of A vs. time is given. Answer the following questions:
   i) What is the order of the reaction?
   ii) What is the slope of the line equal to? S
   iii) What is the unit of the rate constant?



3. Derive an integrated rate equation for the rate constant of a zero order reaction. K

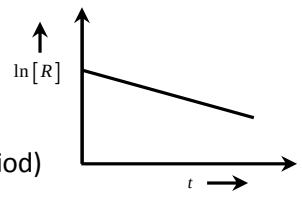
4. Derive an integrated rate equation for the rate constant of a first order reaction. K

5. The initial concentration of N_2O_5 in the following first order reaction $N_2O_5 \longrightarrow 2NO_{2(g)} + \frac{1}{2} O_{2(g)}$ was 1.24×10^{-2} M at 318 K. The concentration of N_2O_5 after 60 minutes was 0.2×10^{-2} M. Calculate the rate constant of the reaction at 318K. [A: k = 0.304] S

6. A first order reaction takes 40 minutes for 30% completion. Calculate the rate constant. [A: k = 0.0089 min^{-1}] S

7. The rate constant of a first order reaction is 3×10^{-3} s^{-1}. Calculate the concentration of the reactant after 30 minutes if the initial concentration is 0.5 M. [A: 0.00228 M] S

8. A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion? [A:160.9 min]	S
9. The rate constant of a first order reactions 3×10^{-4} s^{-1}. What percentage of the reactant will decompose in one hour? [A:66%]	S
10. Show that the time required for 99% completion of a first order reaction is twice the time required for completion of 90% of the reaction.	S
11. The rate constant of a first order reaction is 60 s^{-1}. How much time will it take for the reaction to reduce the initial concentration of the reactant to $1/16^{th}$ of its initial value? [A: 4.62×10^{-2} s]	S
12. The first order rate constant for the decomposition of ethyl iodide at 600K is 1.6×10^{-5} s^{-1}. Its activation energy is 209 kJ/mol. Calculate the rate constant of the reaction at 700K. [A: 6.353×10^{-3} s^{-1}]	S
13. What is the effect of catalyst on a reaction with respect to its i) energy of activation ii) ΔG of the reaction iii) time required for 50% of the reaction to be completed?	A
Five mark questions:	
1. a) The rate constants of a reaction at 500K and 700K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the energy of activation of the reaction. [A:18.23 kJ mol^{-1}] b) What is pseudo first order reaction? Give an example.	S
2. a) The graph of log k vs. 1/T for a reaction is linear with intercept of 10 and slope of -5.1×10^3. Calculate the frequency factor and E_a of the reaction. R = 8.314 $JK^{-1}mol^{-1}$ [A: Frequency factor : 10^{10}, E_a = 97.65 kJ] b) A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction? Explain.	S
3. For a certain chemical reaction, variation in the concentration ***l*n[R] vs time** plot is given: For this reaction write/draw i) order of the reaction? ii) the units of rate constant k? iii) Give the relationship between k and $t_{1/2}$ (half-life period) iv) What does the slope of the line indicate? v) Draw the plot of $\left\{\log\frac{[R_0]}{R}\right\}$ vs. time	S



4. a) Explain collision theory of reaction rate.

   b) Draw a graph of potential energy vs. reaction co-ordinate to show the effect of catalyst on the activation energy. S

5. a) Hydrogen peroxide ($H_2O_{2\,(aq)}$) decomposes to $H_2O_{(l)}$ and $O_{2\,(g)}$ in a reaction that is of first order in H_2O_2 and has a rate constant k = 1.06×10^{-3} min. How long will it take for 15% of a sample of H_2O_2 to decompose? [A: $t_{15\%}$ =153.4 min]

   b) Mention two criteria for effective collision. S

6. a) Distinguish between molecularity and order of a reaction.

   b) The activation energy for the reaction $2HI_{(g)} \longrightarrow H_{2(g)}+I_{2\,(g)}$ is 209.5 kJ/mol at 581 K. Calculate the fraction of molecules having energy equal to or greater than activation energy (R = 8.314 $Jk^{-1}\,mol^{-1}$) [A: 1.471×10^{-19}] S

7. In a pseudo first order hydrolysis of ester in water the following results are obtained.

t in seconds	0	30	60	90
Ester (M)	0.55	0.31	0.17	0.085

   i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

   ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

   [A: (i) 4.67 $\times$ 10^{-3} mol $L^{-1}\,s^{-1}$ (ii) 1.91 $\times 10^{-2}\,s^{-1}$] S

8. a) Rate constant k of a reaction varies with temperature T according to the equation $\log k = \log A - \frac{E_a}{2.303R}\left[\frac{1}{T}\right]$

   When a graph is plotted for log k vs. $\frac{1}{T}$ a straight line with slope -4250 is obtained. Calculate E_a for the reaction (R =8.314 $Jk^{-1}\,mol^{-1}$) [A: 813.75 $kJmol^{-1}$]

   b) For the reaction 2A + B $\longrightarrow$ Products, rate = $k[A]^2[B]$, the rate constant is $4x10^{-5}$ $mol^{-2}\,L^2s^{-1}$. Calculate the initial rate of the reaction when [A] = 0.5 M and [B]=0.3 M. [A: 3×10^{-6} M sec^{-1}] S

9. a) Sucrose decomposes in an acid solution, following first order kinetics. Half – life for the reaction is 3 hrs. Calculate the fraction of sucrose that remains after 8 hrs. [A: 0.1576]

   b) What is the effect of temperature on the (i) rate constant and (ii) $t_{1/2}$ of a reaction. S

10. Following data was obtained for the reaction : A + B $\longrightarrow$ P.

Experiment	[A]M	[B]M	Initial rate [R_o] for appearance of product P
1	0.2	0.3	2×10^{-3} mol $L^{-1}s^{-1}$
2	0.2	0.1	2×10^{-3} mol $L^{-1}s^{-1}$
3	0.4	0.3	$4x\ 10^{-3}$ mol $L^{-1}s^{-1}$

i) What is the order of the reaction with respect to A and B?

ii) Write the rate law. iii) What is the rate constant.

iv) What is the half-life of the reaction.

S