CHEMISTRY

BOOKS - PRADEEP CHEMISTRY (HINGLISH)

CHEMICAL KINETICS

PROBLEM

1. Ammonia and oxygen react at high temperature as:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

In an experiment, the rate of formation of NO is $3.6 \times 10^{-3} Ms^{-1}$. Calculate (a) the rate of disappearance of ammonia and (b) the rate of formation of water.

2. The reaction, $2N_2O_s(g) \Leftrightarrow 4NO_2(g) + O_2(g)$ was studied in a closed vessel It was found that the concentration of NO_2 increases by $2 \cdot 0 \times 10^{-2} \text{mol} \quad L^{-1}$ in five seconds. Calculate

(i) the rate of reaction (ii) the rate of change of concentration of N_2O_5.

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3. For an elementary, $2A + B \rightarrow 3C$, the rate of appearance of C at time 't' is $1 \cdot 3 \times 10^{-4} \text{mol} \quad L^{-1} s^{-1}$. Calculate at this time (i) rate of the reaction (ii) rate of disappearance of A.

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4. For the decomposition of dinitrogen pentoxide at $200^\circ C$,

$N_2O_5(g) \rightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$,

if the intial pressure is 14 mm and after 25 minutes of the reaction, total pressure of the gassous mixture is 133 mm, calculate the average rate of reaction in (a) atm $\overset{-1}{\min} \quad (b) \quad \text{mol} \quad L^{-1} s^{-1}$.

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5. From the concentrations of C_4H_9Cl (butyl chloride) at different times given below, calculate the average rate of the reaction:

$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$

during different intervals of time.

t/s	0	50	100	150	200	300	400
$[C_4H_9Cl]/\text{mol}^{-1}$	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439

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6. The decompoistion of N_2O_5 in CCI_4 solution at $318K$ has been studied by monitoring the concentration of N_2O_5 in the solution. Initially, the concentration of N_2O is $2.33M$ and after 184 min , it is reduced to $2.08M$. The reaction takes place according to the equation:

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Calculate the average rate of this reaction in terms of hours, minutes, and seconds. What is the rate of Production of NO_2 during this period?

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7. For a homogeneous decomposition of N_2O_5 into NO_2 and O_2,

$$2N_2O_5(g) \to 4NO_2(g) + O_2(g), \quad \text{rate} = \frac{-\frac{1}{2}\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]$$

Find out the order with respect to N_2O_5.

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8. Calculate the overall order of a reaction which has the rate expression :

(a) Rate $= k[A]^{1/2}[B]^{3/2}$ $\quad (b) \quad \text{Rate} = k[A]^{3/2}[B]^{-1}$

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9. The rate law for a reaction is found to be : Rate

$= k[NO_2^-][I^-][H^+]^2$

How would the rate of reaction change when (i) Concentration of H^+ is doubled

(ii) Concentration of I^- is halved (iii) Concentration of each of NO_2^-, I^- and H^+ are tripled?

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10. The rate of a gaseous reaction is halved when the volume of the vessel is doubled. What is the order of reaction ?

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11. For the reaction, $2NH_3 \rightarrow N_2 + 3H_2$

if $\dfrac{-d[NH_3]}{dt} = k_1[NH_3]$,

$\dfrac{d[N_2]}{dt} = k_2[NH_3]$, $\dfrac{d[H_2]}{dt} = k_3[NH_3]$

then the relation between k_1, k_2 and k_3 is

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12. Identify the reaction order from each of the following rate constant :

(i)

$k = 2 \cdot 3 \times 10^{-5}$ litre $mol^{-1}\sec^{-1}$ $(ii) k = 3 \cdot 1 \times 10^{-4} \sec^{-1}$

(iii) $k = 9 \cdot 3 \times 10^{-4}$mol litre^{-1} sec^{-1}

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13. During the decomposition of a gas on the surface of a solid catalyst, the pressure of the gas at different times was observed to be as follows :

t/s	0	100	200	300
p/Pa	$5 \cdot 00 \times 10^3$	$4 \cdot 20 \times 10^3$	$3 \cdot 40 \times 10^3$	$2 \cdot 60 \times 10$

Calculate order, rate constant and half-life period of this reaction.

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14. The rate of decomposition of NH_3 on platinum surface, $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ is rate $= k$ order with

$k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. What are the rates of production of N_2 and H_2?

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15. The rate constant for a reaction of zero order in A is $0.0030 mol L^{-1} s^{-1}$. How long will take for the initial concentration to fall from 0.10 M to 0.075 M?

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16. The rate constant for a first order reaction is $60 s^{-1}$. How much time will it take to reduce the initial concentrationof the reactant to its $1/16th$ value ?

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17. The half-life period of a first order reaction is 60 minutes. What percentage will be left after 240 minutes ?

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18. The experimental data for the decomposition of $N_2O_5 [2N_2O_5 \rightarrow 4NO_2 + O_2]$ in gas phase at 318 K are given below :

t/s	0	400	800	1200	1600	2
$10^2 \times [N_2O_5]/molL^{-1}$	$1 \cdot 63$	$1 \cdot 36$	$1 \cdot 14$	$0 \cdot 93$	$0 \cdot 78$	0

(i) Plot $[N_2O_5]$ against time. (ii) Find the half-lif

(iii) Draw a graph between $\log[N_2O_5]$ and t. (iv) What is rate la

(v) Calculate the rate constant. (vi) Calculate the half-life period from k and compare it with (ii).

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19. The rate of formation of a dimer in a second order dimerization reaction is $9.5 \times 10^{-5} molL^{-1}s^{-1}$ at $0.01 molL^{-1}$ monomer concentration. Calculate the rate constant.

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20. The following rate data were obtained at 303K for the following reaction :

$2A + B \rightarrow C + D$

Experiment	$[A]/\text{mol } L^{-1}$	$[B]/\text{mol } L^{-1}$	Initial rate of fo
I	$0 \cdot 1$	$0 \cdot 1$	$6 \cdot 0 \times 10^{-3}$
II	$0 \cdot 3$	$0 \cdot 2$	$7 \cdot 2 \times 10^{-2}$
III	$0 \cdot 3$	$0 \cdot 4$	$2 \cdot 88 \times 10^{-1}$
IV	$0 \cdot 4$	$0 \cdot 1$	$2 \cdot 4 \times 10^{-2}$

What is the rate law ? What is the order with respect to each reactant and the overall order ? Also calculate the rate constant and write its units.

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21. In a reaction between A and B, the initial rate of reaction was measured for different initial concentration of A and B as given below:

A/M	0.20	0.20	0.40
B/M	0.30	0.10	0.05
r_0/Ms^{-1}	5.07×10^{-5}	5.07×10^{-5}	7.6×10^{-5}

22. The rate of a reaction starting with initial concentration of 2×10^{-3} and $1 \times 10^{-3} M$ are equal to 2.40×10^{-40} and $0.60 \times 10^{-4} M s^{-1}$, respectively. Calculate the order of reaction w.r.t. reactant and also the rate constant.

23. The half-life periof of a substance is 50 min at a certain initial concentration. When the concentration is reduced to one-half of its initial concentration, the half-life periof is found to be 25 min. Calculate the order of reaction.

24. Predict the order of the reaction in the given plots :

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25. form the following data for the decompoistion of N_2O_5 in carbon tertrachloride solution at $321K$, show that the reaction is of the first order and calculate the rate constant.

Time (in min) evolved	10	15	20	25	∞
Volume of O_2 (mL)	6.30	8.95	11.40	13.50	34.75

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26. The decomposition of N_2O_5 in $\mathbb{C}l_4$ solution follows the first order rate law. The concentrations of N_2O_5 measured at different intervals are given below :

Time in seconds (t)	0	80	160	410	600	113[illegible]
$[N_2O_5]$ mol / L	5.5	5.0	4.8	4.0	3.4	2.4

Calculate the rate constant at t = 410 s and t = 1130 s. What do these results show ?

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27. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order :

t	0	10	20
x	46.1	29.8	19.3

where t is the time in minutes and x is the volume of standard $KMnO_4$ solution in cm^3 required for titrating the same volume of the reaction mixture.

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28. 1.0 ml of ethyl acetate was added to 25 ml of N/2 HCl. 2 ml of the mixture were withdrawn from time to time during the progress of the hydrolysis of the ester and titrated against standard NaOH solution. The amount to NaOH required for titration at various intervals is given below :

Time (min)	:	0	20	75	119	1
NaOH used (ml)	:	20.24	21.73	25.20	27.60	3

The value at ∞ time was obtained by completing the hydrolysis on boiling. Show that it is a reaction of the first order and find the average value of the velocity constant.

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29. The hydrolyiss of methyl acetate in aqueous solution is has been studied by titrating the liberated acetic acid against $NaOH$. The concentration of ester at different times is given below:

t (min)	0	30	60	90
$C(MolL^{-1})$	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant $(55 molL^{-1})$ during the course of the reaction . What is the value of k' in the equation ?

Rate $= k'[CH_3COOCH_3][H_2O]$

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30. The inverison of cane sugar was studied is HCl at $298K$. The following polarimetric readings were obtained at different intervals of time:

Time (min)	0	7.18	18.00	27.05	∞
Reading (degree)	+24.09	+21.41	+17.74	+15.00	–10.74

Show that the inverison of cane sugar is a unimolecular reaction.

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31. At 373 K, the half-life period for the thermal decomposition of N_2O_5 is 4.6 sec and is independent of the initial pressure of N_2O_5. Calculate the specific rate constant at this temperature.

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32. 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.

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33. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

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34. Show that in case of a first order reaction, the time required for 99.9% of the reaction to take place is about 10 times that the required for half the reaction.

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35. The reaction $SO_2Cl_2 \xrightarrow{k_1} SO_2 + Cl_2$ is a first order reaction with $k_1 = 2.2 \times 10^{-5} s^{-1}$ at $575K$. What percentage of SO_2Cl_2 will get decomposed in 90 min when the reaction is carried out at $575K$.

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36. The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + 1/2O_2$ was $1.24 \times 10^{-2} \text{mol L}^{-1}$ at 318 K. The concentration of N_2O_5 after 60 minutes was $0.20 \times 10^{-2} \text{mol L}^{-1}$. Calculate the rate constant of the reaction at 318 K.

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37. A first order reaction has a specific reaction rate of $10^{-3}\ \sec^{-1}$. How much time will it take for 10 g of the reactant to reduce to 2.5 g ? Given $\log 2 = 0.301, \log 4 = 0.6021, \log 6 = 0.778$.

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38. The decomposition of $\mathrm{N_2O_5}(g), i.e.\ , \mathrm{N_2O_5}(g) \rightarrow 4\mathrm{NO_2}(g) + \mathrm{O_2}(g)$ is a first order reaction with a rate constant of $5 \times 10^{-4} \sec^{-1}$ at $45^\circ C$. If intial concentration of $\mathrm{N_2O_5}$ is 0.25 M, calculate its concentration after 2 min. Also calculate half life for the decomposition of $\mathrm{N_2O_5}(g)$.

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39. The rate constant for an isomerisation reaction $A \rightarrow B$ is $4.5 \times 10^{-3}\ \text{min}^{-1}$. If the initial concentration of A is 1M, Calculate the rate of the reaction after 1 hour.

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40. The following data were obtained the first order thermal decomposition of $N_2O_5(g)$ at constant volume :

$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$

S. No.	Time/s	Total pressure (atm)
1	0	0.5
2	100	0.512

Calculate the rate constant.

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41. AT 373 K, a gaseous reaction A $\rightarrow$ 2B + C is found to be of first order. Starting with pure A, the total pressure at the end of 10 min. was 176 mm and after a long time when A was completely dissociated, it was 270 mm.

The pressure of A at the end of 10 minutes was :

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42. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

(i) After 50 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 sec of decomposition at this temperature.

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43. The rate of a first order reaction is 0.04 mol $\text{litre}^{-1}s^{-1}$ after 10 minutes and 0.03 mol $\text{litre}^{-1}s^{-1}$ after 20 minutes. Find the half life period of the reaction.

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44. One-fourth of a first order reaction is completed in 32 minutes. What is the half-life period of this reaction?

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45. After 24 hours, only 0.125 g out of the initial quantity of 1 g of a radioactive isotope remains behind. What is its half-life period ?

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46. Half-life period of a radioactive element is 100 seconds. Calculate the disintegration constant and average life. How much time will it take to lose its activity by 90% ?

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47. The rate constant of a reaction is $1.2 \times 10^{-3} \sec^{-1}$ at $30^\circ C$ and $2.1 \times 10^{-3} \sec^{-1}$ at $40^\circ C$.

Calculate the energy of activation of the reaction.

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48. The rate of a particular reaction doubles when temperature changes from 27° C to $37^\circ C$. Calculate the energy of activation of such a reaction.

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49. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at $40^\circ C$ is $1.8 \times 10^{-1} \sec^{-1}$. Calculate the frequency factor A.

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50. The first order rate constant for the decompoistion of C_2H_5I by the reaction.

$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$

at $600K is 1.60 \times 10^{-5} s^{-1}$. Its energy of activation is $209 kJ mol^{-1}$. Calculate the rate constant at $700K$

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51. Rate constant k of a reaction varies with temperature according to the equation

$\log k = \text{ constant } - \frac{E_a}{2.303}. \frac{1}{T}$

where E_a is the energy of activation for the reaction. When a graph is plotted for log k versus $1/T$, a straight line with a slope -6670 K is obtained. Calculate the energy of activation for this reaction. State the units $\left(R = 8.314 \text{ JK}^{-1} mol^{-1}\right)$

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52. The rate constant of a reaction of a reaction increases by 5% when the temperature of the reaction is increased from 300 to 301 K where equilibrium constant increases only by 2% . Calculate the activation energy for the forward as well as backward reaction.

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53. At $27^{\circ}C$ in the presence of a catalyst, the activation ?energy of a reaction is lowered by 2 kcal. Calculate by how much the rate of reaction will increase ?

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54. A hydrogenation reaction is carried out at 500 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 energy by 20 kJ mol^{-1} .

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55. The rate constants of a reaction at 500 K and 700 K are $0.02s^{-1}$ and $0.07s^{-1}$ respectively. Calculate the values of E_a and A.

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PROBLEMS FOR PRACTICE

1. For the reaction $2 \text{ X} \rightarrow \text{X}_2$, the rate reaction becomes 27 times when the concentration of X is increased three times. What is the order of the reaction ?

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2. A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when (i) the concentration of B alone is increased to three times (ii) the concentrations of A as well as B are doubled?

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3. Show by uisng rate laws how much the rate of reaction $2NO(g) + O_2(g) \rightarrow 2NO(g)$ will change if the volume of the reaction vessel is diminished to $1/3$ of its initial volume.

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4. The rate constant of a reaction is $3 \times 10^2 hr^{-1}$. What is the order of the reaction?

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5. In the reaction $A \rightarrow B$, the value of the rate constant was found to be $1.0 \times 10^{-2} mol^{-1} \mathrm{L} \ \ s^{-1}$. What is the order of the reaction ? How will the catalyst affect the value of the rate constant ?

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6. The rate of reaction $A + B \rightarrow$ Products is given by Rate $= k[A]^{1/2}[B]^2$. What are the units of the rate constant ?

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7. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half ? What is the unit of rate constant of such a reaction ?

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8. What are the units of rate constant for zero order and first order reactions ?

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9. In the following reaction:

$$2NO(g) + O_2(g) \xrightarrow{k'} 2NO_2(g)$$

What is the predicted rate law, if the mechanism is

$NO + O_2(g) \overset{k_{eq}}{\Longleftrightarrow} NO_3(\text{fast})$ (fast)

$NO_3 + NO \xrightarrow{k_1} NO_2 + NO_2$ (slow)

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10. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimentally determined rate expression below 400 K is rate = $k[NO_2]^2$. What mechanism can be proposed for this reaction ?

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11. For the chemical reaction, $4\ \mathrm{HBr} + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O} + 2\ \mathrm{Br}_2$, Rate $= k[\mathrm{HBr}][\mathrm{O}_2]$.

What is the probable mechanism of the reaction ?

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12. Nitric oxide reacts with hydrogen to give nitrogen and water $(2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O)$. The kinetics of this reaction is explained by the following steps :

(i)

$2NO + H_2 \rightarrow N_2 + H_2O_2(\text{slow})$ (ii) $H_2O_2 + H_2 \rightarrow 2\ H_2O(\text{fast})$

What is the predicted rate law ?

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13. For the reaction at 500 K, $NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$, the proposed mechanism is as below :

(i)

$NO_2 + NO_2 \rightarrow NO + NO_3(\text{slow})$ (ii) $NO_3 + CO \rightarrow CO_2 + NO_2(\text{fa$

What is the rate law for the reaction ?

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14. The possible mechanism for the reaction :

$2\ H_2 + 2\ NO \rightarrow N_2 + 2\ H_2O$ is (i)

$2NO \Leftrightarrow N_2O_2$ (ii) $N_2O + H_2O(\text{slow})$ (iii) $N_2O + H_2 \rightarrow N_2 + H_2O(\text{fa}$

What is (i) the rate law for the reaction

(ii) the order of the reaction ?

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15. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions :

$2\ H_2O_2 \xrightarrow{OH^-} 2\ H_2O + O_2$

This reaction takes place in two steps as given below :

Step-I. $H_2O_2 + I^- \rightarrow H_2O + IO^-(\text{slow})$

Step-II. $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2(\text{fast})$

(a) Write the rate law expression and determine the order of reaction w.r.t. H_2O_2.

(b) What is the molecularity of each individual step ?

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16. The decomposition of N_2O_5 in a carbon tetrachloride solutioin has been investigated.

$N_2O_5(\text{solution}) \rightarrow 2NO_3$ (solution) +$1/2O_2(g)$ ltrbgt The reaction has been found to be of the first order in N_2O_5 with a first order rate-constant = $6.2 \times 10^{-4} s^{-1}$. Calculate the rate of the reaction when (a) $[N_2O_5]$ = 1.25 mol L^{-1} and b) $[N_2O_5]$ = 0.25 mol L^{-1}. c) What concentration of N_2O_5 would give a rate of $2.4 \times 10^{-3} mol L^{-1} s^{-1}$?

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17. For the following reaction:

$2A + B + C \rightarrow A_2B + C$

The rate law has been determined to be

Rate $= k[A][B]^2$ with $k = 2.0 \times 10^{-6} mol^{-2} L^2 s^{-1}$

For this reaction, determine the initial rate of the reaction with $[A] = 0.1 mol L^{-1}$, $[B] = 0.2 mol L^{-1}$, $C = 0.8 mo, L^{-1}$. Determine the rate after $0.04 mol L^{-1}$ of A has reacted.

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18. Following data are obtained for the reaction

$$N_2O_5 \to 2NO_2 + \frac{1}{2}O_2$$

$$N_2O_5 \longrightarrow 2\,NO_2 + \frac{1}{2}\,O_2$$

t/s	0	300	600
$[N_2O_5]/mol\ L^{-1}$	$1{\cdot}6 \times 10^{-2}$	$0{\cdot}8 \times 10^{-2}$	$0{\cdot}4 \times 10^{-2}$

(a) Show that it follows first order reaction

(b) Calculate the half-life

(Given $\log 2 = 0.3010, \log 4 = 0.6021$)

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19. For a gaseous reaction $2A + B_2 \to 2AB$, the following rate data were obtained at 300 K

Rate of disappearance of B_2	Concentration	
(mol lit^{-1}min^{-1})	$[A]$	$[B_2]$
$(i)1.8 \times 10^{-3}$	0.015	0.15
$(ii)1.08 \times 10^{-2}$	0.09	0.15
$(iii)5.4 \times 10^{-3}$	0.015	0.45

Calculate the rate constant for the reaction and rate of formation of AB when [A] is 0.02 and $[B_2]$ is 0.04 "mol lit"^(-1)" at 300 K".`

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20. For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, the following results have been obtained :

S. No.	$[N_2O_5]$ mol L^{-1}	Rate of disappearance of N_2O_5, mol L^{-1} $\min^{-1}$
1	1.13×10^{-2}	34×10^{-5}
2	0.84×10^{-2}	25×10^{-5}
3	0.62×10^{-2}	18×10^{-5}

(a) Calculate the order of reaction

(b) Write rate law

(c) Calculate rate constant of the reaction.

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21. For the thermal decomposition of acetaldehyde, $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$, the following rate data were obtained :

Experiment	Initial pressure (torr)	Initial rate of increase in tota
1	300	$0.61(r_1)$
2	200	$0.27(r_2)$

Predict the order of reaction.

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22. The initial rate of reaction $A + 5B + 6C \rightarrow 3L + 3M$ has been determined by measuring the rate of disappearance of A under the following conditions :

Expt. No.	$[A]_0 / M$	$[B]_0 / M$	$[C]_0 / M$	Initial rate/M r
1	0.02	0.02	0.02	2.08×10^{-3}
2	0.01	0.02	0.02	1.04×10^{-3}
3	0.02	0.04	0.02	4.16×10^{-3}
4	0.02	0.02	0.04	8.32×10^{-3}

Determine the order of reaction with respect to each reactant and overall order of the reaction. What is the rate constant ? Calculate the initial rate of change in concentration of B and L.

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23. The following data were reported for the decompoistion of N_2O_5 in CCl_4 at $303K$:

Time (min)	120	160	200	240	∞
Vol of$O_2(mL)$	37.70	45.85	52.67	58.34	84.35

Show that the reaction is the first order and calculate the rate constant.

Note: This is an example of direct-estimation of Product, i.e., O_2.

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24. The rate of decomposition of N_2O_5 in CCl_4 solution has been studied at 318 K and the following results have been obtained :

$t/$ min	0	135	342	683	1693
c/M	2.08	1.91	1.67	1.35	0.57

Find the order of the reaction and calculate its rate constant. What is the half-life period ?

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25. The catalysed decomposition of H_2O_2 in aqueous solution is followed by removing equal volume samples at various time intervals and titrating them with $\mathrm{KMnO_4}$ to determine the undecomposed H_2O_2. The results thus obtained are :

Time (seconds)	:	0	600	1200
cm^2 of KMnO	:	22.8	13.8	8.2

Show that the reaction is mono-molecular. What is the value of the specific reaction rate ?

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26. Methyl acetate was subjected to hydrolyiss in $N-HCl$ at $298K$. $5mL$ of the mixture is withdraw at different intervals and titrated with constant with about $N/8NaOH$. The following results were obtained:

Time (min)	0	25	40	61	∞
Vol of alkali used (mL)	19.24	24.20	26.60	29.50	42.1

Show that the reaction is of first order.

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27. A 20% solution of cane sugar having dextrorotation of 34.50 inverted by $0.5N$ lactic acid to at $298K$. The rotations determined are as follows:

Time (min)	0	14.55	111.36	∞
Rotation	34.50	31.10	13.98	-10.77

Show that the inverison of sugar is a unimolecular reaction.

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28. A first order reaction is found to have a rate constant $k = 7.39 \times 10^{-5} s^{-1}$. Find the half life of this reaction.

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29. Time for half change for a first order reaction is 25 minutes. What time will be required for 99% reaction ?

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30. The half life period of a first order reaction is 60 minutes. What percentage of the reactant will be left behind after 120 minutes ?

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31. It was found that a solution of cane sugar was hydrolysed to the extent of 25% in 1 hr. Calculate the time taken for the sugar to be 50% hydrolysed assuming that the reaction is of first order.

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32. Decomposition of a gas is of first order. It takes 80 minutes for 80% of the gas to be decomposed when its initial concentration is 8×10^{-2} mole/litre. Calculate the specific reaction rate.

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33. The data for the conversion of compound A into its isomeride B are as follows :

Time is hr :	0	1	2	3	4	∞
%age of A :	49.3	34.6	25.8	18.5	13.8	4.8

Show that this is a first order reaction.

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34. The following data were obtained during the catalysed decomposition of N_2O at 1173 K :

Time (min)	30	53	63	80	100	120
%age decomposed	32	50	57	65	73	78

Show that the reaction is of the first order and calculate velocity constant of the reaction.

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35. Find the two-thirds life $(t_{2/3})$ of a first order reaction in which $k = 5.48 \times 10^{-1} \sec^{-1}$ (log 3 = 0.4771 , log 2 = 0.3010)

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36. A first order reaction has a rate constant of $1.15 \times 10^{-3} s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g ?

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37. For a first order reaction, calculate the ratio between the time taken to complete three fourth of the reaction and the time taken to complete half of the reaction.

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38. If the rate constant of a first order reaction at a certain temperature is $1.5 \times 10^{-1} s^{-1}$ and t_1 and t_2 are the respective times for 50% and 75% completion of the reaction, determine the ratio of $t_2 \text{ to } t_1$.

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39. For a first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.4 mol L^{-1}. How long in all will it take for the initial concentration to become 0.3 mol L^{-1}?

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40. A first order reaction in 75% complete is 60 minutes. Find the half life of this reaction.

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41. In a hydrolysis reaction, 5 g of ethyl acetate is hydroloysed in the presence of dilute HCl in 300 minutes. If the reaction is of first order and the initial concentration of ethyl acetate is 22g/L, calculate the rate constant for the reaction.

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42. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.

Watch Video Solution

43. A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

(Given $\log 2 = 0.3010, \log 4 = 0.6021$)

Watch Video Solution

44. In a particular reduction process, the concentration of a solution that is initially 0.24 M is reduced to 0.12 M in 10 hours and 0.06 M in 20 hours. What is the rate constant for the reaction?

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45. The following rate data were obtained for the thermal decomposition of $N_2O_5(g)$

$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$

Time (sec)	0	50
Total pressure (atm)	0.2	0.25

Calculate the reaction rate when the total pressure is 0.28 atm

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46. The half-life period of a first order reaction is 600 s. What percent of A remains after 30 minutes ?

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47. 50% of a reaction is completed in 16 minutes. What fraction of the reaction would occur in 32 minutes ? Given that reaction follow first order reaction.

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48. The decomposition of a compound is found to follow the first order rate law. If it takes 15 minutes for 20 per cent of the original material to react, calculate

i) the specific rate constant

ii) the time in which 10 percent of the original material remains unreacted.

iii) The time it takes for the next 20 percent of the reactant left to react.

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49. A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete.

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50. 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

?

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51. Rate constant of a first order reaction, A $\rightarrow$ Product is 0.016 min^{-1}. Calculate the time required for 80% of the reaction to be completed.

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52. A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, What concentration of reactant will remain in solution after 3 hours?

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53. A first order reaction has $k = 1.5 \times 10^{-6}$ per second at $240^{\circ} C$. If the reaction is allowed to run for 10 hours, what percentage of initial concentration would have changed to products ? What is the half-life period of this reaction ?

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54. The thermal decomposition of formic acid (HCOOH) is a first order reaction with the rate constant of $2.4 \times 10^{-3} s^{-1}$ at a certain temperature.Calculate how long will it take for three-fourth of initial quantity of HCOOH to decompose.

Watch Video Solution

55. The rate constant of a first order reaction is $60 s^{-1}$. How much time it will take to reduce 75% of its original concentration ?

Watch Video Solution

56. The rate constant of a first order reaction is $60s^{-1}$. How much time it will take to reduce 75% of its original concentration ?

Watch Video Solution

57. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.

(Given, $\log 2 = 0.3010, \log 3 = 0.4771, \log 4 = 0.6021$)

Watch Video Solution

58. The following data were obtained during the first order thermal decompostion of SO_2CI_2 at a constant volume :

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate rate constant

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59. The rate constants of a reaction are $1 \times 10^{-3} \sec^{-1}$ and $2 \times 10^{-3} \sec^{-1}$ at $27^{\circ} C$ and $37^{\circ} C$ respectively. Calculate the activation energy of the reaction.

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

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61. The rate of a reaction triples when temperature changes from 50 to $100^{\circ} C$. Calculate the energy of activation for such a reaction $\left(R = 8.314 \ \text{J K}^{-1} \ \text{mol}^{-1}\right)$

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62. For a reaction, the activation energy is zero. What is the value of rate constant at $300K$ if $k = 1.6 \times 10^6 s^{-1}$ at 280 K $(R = 8.31 JK^{-1} mol^{-1})$?

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63. The activation energy of a first order reaction at 300 K is 60 kJ mol^{-1}. In the presence of a catalyst, the activation energy is lowered to 50 kJ mol^{-1} at the same teperature. How many times the rate of reaction will change ?

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64. Given that the temperature coefficient for the saponification of ethylacetate by $NaOH$ is 1.75. Calculate the activation energy.

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65. The activation energy of the reaction is $75.2 kJmol^{-1}$ in the absence of a catalyst and $50.14 \text{ kJ mol}^{-1}$ with a catalyst. How many times will the rate of reaction grow in the presence of the catalyst if the reaction proceeds at $25^\circ C$? $\left(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}\right)$.

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66. The rate constants of a reaction at 700 K and 760 K are $0.011 \text{ M}^{-1} s^{-1}$ and $0.105 \text{ M}^{-1} s^{-1}$ respectively.

Calculate the values of Arrhenius parameters.

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67. A 1st order reaction is 50% complete in 30 minutes at $27^\circ C$ and in 10 min at $47^\circ C$. Calculate

(i) rate constant for the reaction at $27^\circ C$ and $47^\circ C$

(ii) energy of activation for the reaction.

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68. Nitrogen dioxide (NO_2) reacts with fluroine (F_2) to form nitryl fluroide (NO_2F) according to the reaction.

$2NO_2(g) + F_2 \rightarrow 2NO_2F(g)$

Write the instaneous rate of reaction in terms of

i) rate of formation of NO_2F,

ii) Rate of disappearance of NO_2,

iii) rate of disappearance of F_2

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69. Express the relationship between the rate of production of water and the rate of disappearance of oxygen in the reaction :

$2\ \mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2H_2O$

Watch Video Solution

70. For the reaction, $4\ \mathrm{NH_3}(g) + 5\ \mathrm{O_2}(g) \rightarrow 2NO(g) + 6H_2O(g)$, if the rate expression in terms of disappearance of NH_3 is $-\frac{\Delta[NH_3]}{\Delta t}$, write the rate expression in terms of concentration of O_2 and H_2O.

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71. A reaction $2\ \mathrm{X} \rightarrow \mathrm{Y}\ + 3Z$ (e.g., $2NH_3 \rightarrow N_2 + 3H_2$) is being carried out in a closed vessel. The rate of disappearance of X, $-\frac{\Delta[X]}{\Delta t}$ is found to be $0.066\ \mathrm{mol\ L}^{-1} s^{-1}$. Calculate $\frac{\Delta[Y]}{\Delta t}$ and $\frac{\Delta[Z]}{\Delta t}$

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72. A chemical reaction $2A \rightarrow 4B + C$ in gas phase occurs in a closed vessel. The concentration of B is found to increase by 5×10^{-3} mol L^{-1} in 10 seconds. Calculate i) the rate of appearance of B ii) the rate of disappearance of A.

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73. $\mathrm{A} \ +2 \ \mathrm{B} \rightarrow 3 \ \mathrm{C}+2 \ \mathrm{D}$. The rate of disappearance of B is $1 \times 10^{-2} \ \mathrm{mol\,lit}^{-1}\mathrm{sec}^{-1}$. What will be (i) Rate of the reaction (ii) Rate of change in concentration of A and C ?

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CURIOSITY QUESTION

1. Pieces of wood burn faster than a log of wood of the same mass because

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2. Carbon of the coal can combine with oxygen of air to form CO, CO_2 etc. (i.e., ΔG is - ve are the reaction is thermodynamically feasible). Then why if does not happen unless a flame is applied to start combustion, though O_2 is available in abundance ?

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TEST YOUR GRIP (MULTIPLE CHOICE QUESTIONS)

1. In the reaction,

$BrO_3^-(aq) + 5Br^-(aq) + 6\ H^+ \rightarrow 3\ Br_2(l) + 3\ H_2O(l)$,

the rate of appearance of bromine (Br_2) is related to the rate of disappearance of bromide ions as follows :

A. $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$

B. $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$

C. $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$

D. $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

Answer: D

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2. Time required for 100 percent completion of a zero order reaction is

A. $\frac{2k}{a}$

B. $\frac{a}{2k}$

C. $\frac{a}{k}$

D. a k

Answer: C

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3. For the reaction $aA+bB\to cC$, if $-3\frac{d[A]}{dt}=-\frac{d[B]}{dt}=+1.5\frac{d[C]}{dt}$, then a, b and c respectively are

A. 3, 1, 2

B. 2, 1, 3

C. 1, 3, 2

D. $6, 2, 3$

Answer: C

Watch Video Solution

4. The rate of a gaseous reaction is given by the expression k [A] [B]. If the volume of the reaction vessel is suddenly reduced to $1/4th$ of the initial volume, the reaction rate relating to original rate will be

A. $1/10$

B. $1/8$

C. 8

D. 16

Answer: D

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5. In a reaction $A \rightarrow B$ the rate of reaction increases two times on increasing the concentration of the reactant four times, then order of reaction is

A. 0

B. 2

C. $1/2$

D. 4

Answer: C

Watch Video Solution

6. The rate of the reaction

$2NO + CI_2 \rightarrow 2NOCI$

is given by the rate equation

$Rate = k[NO]^2[CI_2]$

The value of the rate constant can be increased by

A. increasing the temperature

B. increasing the concentration of NO

C. increasing the concentration of Cl_2

D. doing all of these

Answer: A

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7. The unit of rate constant for a zero order reaction is

A. $\text{mol L}^{-1}s^{-1}$

B. $\text{L mol}^{-1}s^{-1}$

C. $\text{L}^2 mol^{-2}s^{-1}$

D. s^{-1}

Answer: A

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8. A first order reaction has a half-life period of 34.65 seconds. Its rate constant is

A. $2 \times 10^{-2} \sec^{-1}$

B. $4 \times 10^{-4} \sec^{-1}$

C. $20 \sec^{-1}$

D. $2 \times 10^{-4} \sec^{-1}$

Answer: A

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9. Rate constant of a reaction (k) is $175 \text{litre}^2 \text{mol}^{-2} \sec^{-1}$. What is the order of reaction ?

A. first

B. second

C. third

D. zero

Answer: C

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10. The molecularity and order of the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ are respectively

A. one and one

B. two and two

C. three and three

D. two and three

Answer: C

Watch Video Solution

11. Consider the reaction,

$$Cl_2(aq) + H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is,

Rate $= k[Cl_2][H_2S]$

Which of these mechanisms is / are consistent with this rate equation ?

(I) $Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)

$Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$ (fast)

(II) $H_2S \Leftrightarrow H^+ + HS^-$ (fast equilibrium)

$Cl^+ + HS^- \rightarrow 2Cl^- + H^+ + S$ (slow)

A. Neither A nor B

B. A only

C. B only

D. Both A and B

Answer: B

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12. The plot of concentration of the reactant vs time for a reaction is a straight line with a negative slope. This reaction follows

A. Second order

B. Third order

C. First order

D. Zero order

Answer: D

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13. The reaction A $\rightarrow$ B follows first order reaction. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 moles of B?

A. 1 hour

B. 0.5 hour

C. 0.25 hour

D. 2 hours

Answer: A

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14. The rate of a chemical reaction doubles for every $10^{\circ} C$ rise of temperature. If the temperature is raised by $50^{\circ} C$, the rate of the reaction increases by about

A. 24 times

B. 32 times

C. 64 times

D. 10 times

Answer: B

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15. If 75% of first order reaction is completed in 32 min, then 50% of the reaction would be complete in:

A. 24 min.

B. 8 min.

C. 16 min.

D. 4 min.

Answer: C

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16. $1/[A]$ versus time is a straight line, the order of reaction is

A. 1

B. 2

C. 3

D. 0

Answer: B

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17. The rate constant, the activation energy and the Arrhenius parameter of a chemical reactions at $25^{\circ} C$ are $3.0 \times 10^{-4} s^{-}$, $104.4 \text{ kJ mol}^{-1}$ and $6 \times 10^{14} s^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is

A. $2.0 \times 10^{18} s^{-1}$

B. $6.0 \times 10^{14} s^{-1}$

C. Infinity

D. $3.6 \times 10^{30} s^{-1}$

Answer: B

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18. If a graph is plotted between ln k and $1/T$ for the first order reaction, the slope of the straight line so obtained is given by

A. $-\frac{E_a}{R}$

B. $-\frac{E_a}{2.303R}$

C. $-\frac{2.303}{E_aR}$

D. $-\frac{E_a}{2.303}$

Answer: A

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19. A chemical reaction was carried out at 300 K and 280 K. The rate constants were found to be k_1 and k_2 respectively. Then

A. $K_2 = 4K_1$

B. $K_2 = 2K_1$

C. $K_2 = 0.25K$

D. $K_2 = 0.5K_1$

Answer: C

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20. Collision theory is applicable to

A. First order reactions

B. Zero order reactions

C. Bimolecular reactions

D. Intramolecular reactions

Answer: C

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21. 10 g of a radioactive isotope is reduced to 1.25 g in 12 years. Therefore half-life period of the isotope is

A. 24 years

B. 4 years

C. 3 years

D. 8 years

Answer: B

Watch Video Solution

22. The half-life period of a redioactive element is 20 days. What will be the remaining mass of 100 g of it after 60 days ?

A. 25 g

B. 50 g

C. 12.5 g

D. 20 g

Answer: C

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23. The chemical reactions in which the reactants require high amount of activation energy are generally

A. slow

B. fast

C. instantaneous

D. none of these

Answer: A

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24. If the activation enery for the forward reaction is $150 \mathrm{kJ} \mathrm{~mol}^{-1}$ and that of the reverse reaction is $260 \mathrm{kJ} \mathrm{~mol}^{-1}$. What is the ethalpy change for the reaction ?

A. 410 $\mathrm{kJ} \mathrm{~mol}^{-1}$

B. $-110 \quad \mathrm{kJ} \mathrm{~mol}^{-1}$

C. $110 \quad \mathrm{kJ} \mathrm{~mol}^{-1}$

D. $-410 \quad \mathrm{kJ} \mathrm{~mol}^{-1}$

Answer: B

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25. When ethyl acetate was hydrolyzed in the presence of $0.1 M HCl$, the constant was found to be $5.40 \times 10^{-5} s^{-1}$. But when $0.1 M H_2SO_4$ was used for hydrolyiss, the rate constant found to be $6.20 \times 10^{-5} s^{-1}$. form these we can say that

A. H_2SO_4 is stronger than HCl

B. H_2SO_4 is weaker than HCl

C. Both the acids have equal strength

D. The data is insufficient to compare the strengths of HCl and H_2SO_4

.

Answer: A

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TEST YOUR GRIP (FILL IN THE BLANK)

1. For a gaseous reaction, the units of the rate of reaction are.................... .

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2. In the plot of concentration of reactant versus time, the tangent at any instant of time has a .... Slope (positive or negative or zero).

Watch Video Solution

3. If the rate of reaction, $4\ \mathrm{NH}_3 + O_2 \rightarrow 4\ \mathrm{NO} + 6\ \mathrm{H}_2O$ at any instant of time is $9 \times 10^{-4} \mathrm{mol\,L}^{-1} s^{-1}$, then rate of disappearance of NH_3 is................. .

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4. The rate of reaction when the concentration of each reactant is taken as unity is called ....

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5. In the reaction, $2\ \mathrm{NO}_2(g) + F_2(g) \rightarrow 2\ \mathrm{NO}_2F(g)$, order with respect to NO_2 is..........................and that with respect to F_2 is.................. .

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6. The units of rate constant for reactions of second order are ....

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7. The overall rate of a reaction depends upon the ....

Watch Video Solution

8. Rate constant and rate of reaction have the same units for reactions of ....order.

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9. In the decomposition of ozone, $2O_3 \rightarrow 3O_2$, order with respect to O_3 is..........................and that with respect to O_2 is................. .

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10. For the zero order reaction, A $\rightarrow$ Products, with rate constant k, half-life period is given by $t_{1/2}$ =..................... .

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11. In a first order reaction,the concentration of the reactants decreases..............................with time (linearly or eponentially or sinusoidally).

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12. The half life period of a first order reaction is .... of initial concentration of the reactant and......................proportional to the rate constant.

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13. Average life of a first order reaction is the time in which the concentration of the reactant reduces to..........................of the original concentration.

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14. Doubling the concentration of the reactant doubles the half-life period of the reaction. The order of reaction is ....

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15. Inversion of cane sugar is an example of a..........................reaction.

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16. The difference of energy between activated complex and that of the reactants is called ....

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17. The sum of the activation energy and energy possessed by the reactants is called.......................... .

Watch Video Solution

18. The temperature coefficient of most of the reactions lies between

Watch Video Solution

19. Arrhenius equation is

Watch Video Solution

20. The factor $e^{-E/RT}$ in Arrhenius equation is called.........................factor.

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21. Activation energy of reactions for which rate constant is doubled when the temperature is increased by 10° (from 300 K to 310 K) is nearly...................... .

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22. In the presence of catalyst, activation energy for forward reaction........................, that for backward reaction....................and the value of enthalpy change......................... .

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Watch Video Solution

23. According to collision theory, rate constant, $k = PZ_{AB}e^{-E_a/\mathrm{RT}}$. Here, Z_{AB} represents.............................and P represents...................... .

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CONCEPTUAL QUESTIONS (I. General introduction and rates of reactions)

1. For a reaction $A \to B$, the rate of reaction can be denoted by $-\frac{dA}{dt}$ or $+\frac{dB}{dt}$. State the significance of plus and minus signs in this case.

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2. Why in general a reaction does not proceed with a uniform rate throughout or why instantaneous rate is preferred over average rate ?

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3. Why boiling of an egg or cooking of rice in an open vessel takes more time at a hill station ?

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4. A reaction proceeds with a uniform rate throughout. What do you conclude? Or Is there any reaction whose rate does not decrease with time ?

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5. When is the rate of reaction equal to specific rate constants ?

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6. Following reaction takes place in one step: $2NO + O_2 + 2NO_2$ How will the rate of above reaction change if the volume of reaction vessel is reduced to 1/3 rd of original volume? Will there be any change in the order of reaction?

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CONCEPTUAL QUESTIONS (II. Rate law, order of reaction, rate constant and its units)

1. What is the order of reaction whose rate constant has the same units as rate of reaction ?

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2. Why are reactions of higher order less in number?

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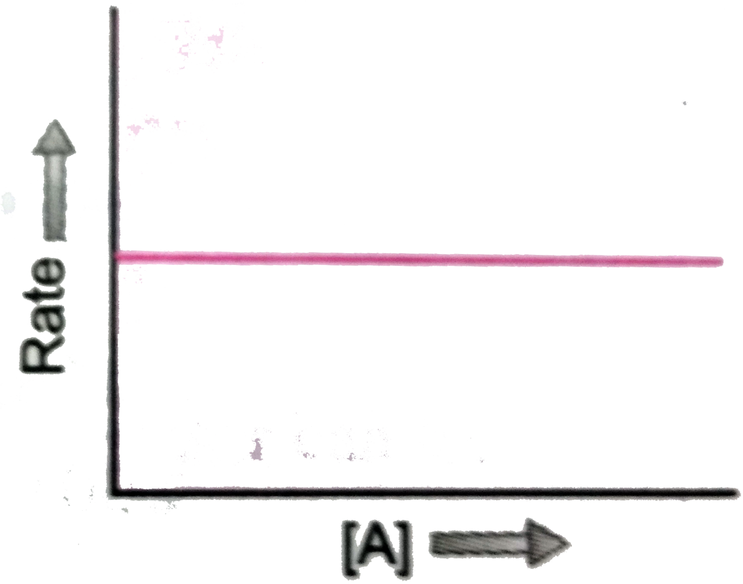
3. For a reaction, the graph of the rate of reaction against molar concentration of the reactant is as shown. What is the order of the reaction ?



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CONCEPTUAL QUESTIONS (III. Molecularity of a reaction, its mechanism and difference between order and molecularity)

1. For a reaction, the rate law is : Rate $= k = [A][B]^{1/2}$. Can this reaction be an elementary reaction ?

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2. The rate expression for the reaction, $(CH_3)C - Cl + OH^- \rightarrow (CH_3)_3C - OH + Cl^-$

is Rate $= k\left[(CH_3)_3C - Cl\right]$. Propose the mechanism for the reaction.

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CONCEPTUAL QUESTIONS (IV. Integrated rate equations, half-life, determination of rate law, rate constant and order)

1. For a certain chemical reaction, variation in the concentration in [R] vs time (s) plot is given in the Fig. :

For this reaction write/draw

(i) what is the order of the reaction ?

(ii) what are 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 ?

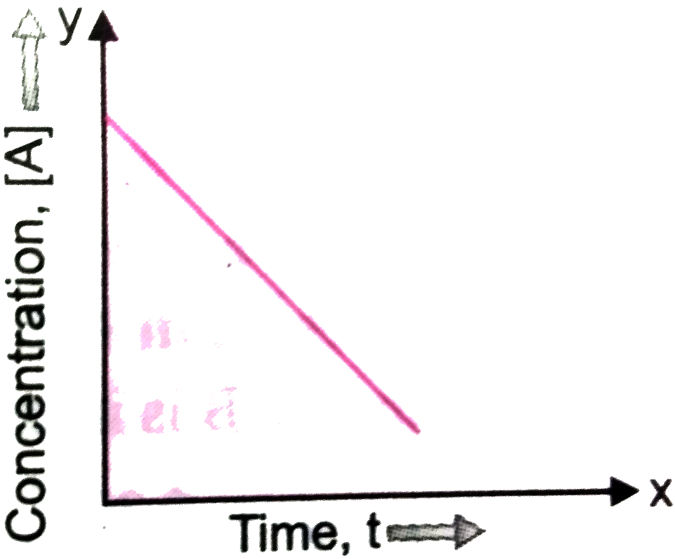
(v) draw the plot log $\{[R]_0/[R]\}$ vs time (s).

View Text Solution

2. Consider the reaction $A \xrightarrow{K}$ P. The change in concentration of A with time is shown in the plot.

(i) Predict the order of the plot.

(ii) Derive the expression for the time required for the completion of the reaction.



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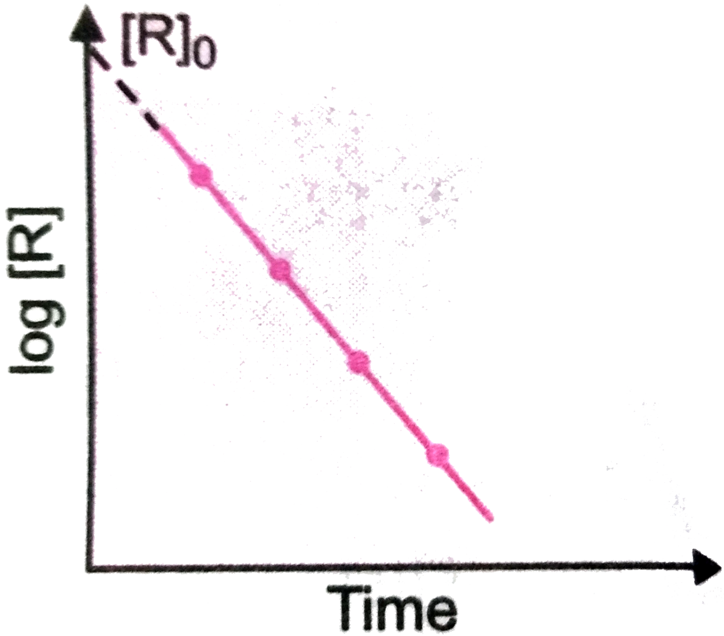
3. Observe the graph in the diagram and answer the following questions :

(i) If slope is equal to $-2.0 \times 10^{6} \sec^{-1}$, what will be the value of rate constant ?

(ii) How does the half-life of zero order reaction relate to its rate constant

?



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4. For a first order reaction, time taken for half of the reaction to complete is t_1 and $\frac{3}{4}$ of the reaction to complete is t_2. How are `t_(1)and t_(2) related?

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5. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?

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6. For a reaction :

$2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

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CONCEPTUAL QUESTIONS (V. First order reactions, pseudo first order reactions and radioactive disintegration)

1. What are the units of the rate constant of a pseudo unimolecular reaction ?

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2. Why hydrolysis of ethyl acetate with NaOH is reaction of second order while with HCl, it is of first order ?

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3. The rate constant for a second order reaction is $k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{(b-x)}$

where a and b are initial concentrations of the two reactants A and B involved. If one of the reactants is present in excess, it becomes pseudo unimolecular. Explain how ?

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CONCEPTUAL QUESTIONS (VI. Activation energy, effect of temp. on rate (Arrhenius eqn.) and effect of catalyst on rate)

1. On the basis of enthalpy of formation, graphite is more stable than diamond, yet diamond does not change into graphite for years. Why ?

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2. The reactions $: 2CO(g) = O_2 9g) \rightarrow 2CO_2(g)$ and $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ look to be similar. Yet the former is slower than latter at same temperature. Why ?

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3. Can a reaction have zero activation energy ?

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4. Can a reaction have negative activation energy?

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5. What is the fraction of molecules having energy equal to or greater than activation energy, E_a ? What is this quantity called ?

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6. What is the value of rate constant at extremely high temperature $(= \infty)$? It this rate constant feasible ? Why or why not ?

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7. Assuming the energy of activation for most of the reactions is 52 kJ, what conclusions you draw about the effect of temperature on the rate of a reaction?

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8. Why equilibrium constant of a reaction does not change in the presence of a catalyst ?

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9. What is the effect of adding catalyst on free energy change (ΔG) of a reaction ?

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CONCEPTUAL QUESTIONS (VII. Collision theory)

1. In some cases, it is found that a large number of colliding molecules have energy more than thereshold value, yet the reaction is slow. Why?

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NCERT QUESTIONS AND EXERCISES WITH ANSWERS (NCERT INTEXT UNSOLVED QUESTIONS & PROBLEMS)

1. For the reaction $R \rightarrow P$, the concentration of reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction rate of reaction using units of time both in minutes and seconds.

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2. In a reaction, $2A \rightarrow$ Products the concentration of A decreases from 0.5 "mol" litre^(-1) $\rightarrow$ 0.4$\text{mol}litre^{-1}$ in 10 minutes. Calculate rate during this interval.

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3. For a reaction, $A+B \rightarrow$ Products, the rate law is given by: $r=k[A]^{1/2}[B]^2$. What is the order of reaction:

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4. The conversion of molecules X to Y follows second order kinetics. If the concenration of X is increased to three times, how will it affect the rate of formation of Y ?

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5. A first order reaction has a rate constant $1.15 \times 10^{-3} s^{-1}$. How long will $5g$ of this reactant take to reduce to $3g$` ?

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6. 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.

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7. What will be effect of temperature on rate constant ?

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8. The rate of the chemical reaction doubles for an increase of 10 K from 298 K. Calculate E_a.

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9. The activation energy for the reaction, $2Hi(g) \rightarrow H_2(g) + I_2(g)$ is 209.5 kJ $moli^{-1}$ at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

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NCERT EXERCISES

1. From the rate expression for the following reactions, determine their order of reaction and dimensions of the rate constants.

$a.\ 3NO(g) \rightarrow N_2O(g)$, Rate $= k[NO]^2$

$b.\ H_2O_2(aq) + 3I^{c-}(aq) + 2H^{\oplus} \rightarrow 2H_2O(l) + I_3^{c-}$, Rate $= k[H_2O_2][I^{c-}]$

$c.\ CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$, Rate $= k[CH_3CHO]^{3/2}$

$d.\ C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$, Rate $k[C_2H_5Cl]$

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2. For the reaction :

$2A + B \rightarrow A_2B$

the rate $= k[A][B]^2$ with $k = 2.0 \times 10^{-6} mol^{-2}L^2s^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 molL^{c-}, [B] = 0.2 molL^{-1}$. Calculate the rate of reaction after $[A]$ is reduced to $0.06 molL^{-1}$.

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3. 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 $k = 2.5 \times 10^{-4} mol^{-1} \mathrm{L\,s}^{-1}$?

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4. The decomposition of dimethyl ether leads to the formation of $CH_4, H_2,$ and CO and the reaction rate is given by

Rate $= k[CH_3OCH_3]^{3/2}$

The rate of reaction is followed by increase in the pressure in a closed vessel , so the rate can also be expressed in terms of the partial pressure of dimethyl either, $i.e.$,

Rate $= k[p_{CH_3OCH_3}]^{3/2}$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant ?

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5. Mention the factors that affect the rate of a chemical reaction.

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6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to $1/2$?

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7. What is the effect of temperature on the rate constant of reaction? How can this temperature effect on the rate constant be represented quantitatively?

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8. In a pseudo first order hydrolysis of ester in water the following result6s were obtained:

t/s	0	30	60	90
$[\text{Ester}]$	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.

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9. A reaction is first order in A and second order in B

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentation of B three times ?

(iii) How is the rate affected when the concentration of both A and B are doubled ?

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10. In a reaction between A and B, the initial rate of reaction was measured for different initial concentration of A and B as given below:

A/M	0.20	0.20	0.40
B/M	0.30	0.10	0.05
r_0/Ms^{-1}	5.07×10^{-5}	5.07×10^{-5}	7.6×10^{-5}

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11. The following rate data were obtained at 303K for the following reaction :

$2A + B \rightarrow C + D$

Experiment	$[A]/\text{mol} \quad L^{-1}$	$[B]/\text{mol} \quad L^{-1}$	Initial rate of fo
I	$0 \cdot 1$	$0 \cdot 1$	$6 \cdot 0 \times 10^{-3}$
II	$0 \cdot 3$	$0 \cdot 2$	$7 \cdot 2 \times 10^{-2}$
III	$0 \cdot 3$	$0 \cdot 4$	$2 \cdot 88 \times 10^{-1}$
IV	$0 \cdot 4$	$0 \cdot 1$	$2 \cdot 4 \times 10^{-2}$

What is the rate law ? What is the order with respect to each reactant and the overall order ? Also calculate the rate constant and write its units.

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12. The reaction between A and B is first order with respect to A and zero with respect to B. Fill in tha blanks in the following table:

Experiment	$[A]/M$	$[B]/M$	Initial rate/M min
$I.$	0.1	0.1	2.0×10^{-2}
$II.$	....	0.2	4.0×10^{-2}
$II.$	0.4	0.4	....
$IV.$	....	0.2	2.0×10^{-2}

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13. Calculate the half life of a first order reaction from their rate constants given below :

(a) $200 \quad s^{-1}$ (b) $2 \quad \min^{-1}$ (c) $4 \quad \text{year}^{-1}$

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14. The half-life for radioactive decay of ^{14}C is 5730 y.

An archaelogical artifact contained wood that had

only 80% of the ^{14}C found in living tree.

Estimate the age of the sample.

Watch Video Solution

15. The experimental data for the decomposition of $N_2O_5[2N_2O_5 \rightarrow 4NO_2 + O_2]$ in gas phase at 318 K are given below :

$$\begin{cases} t/s & 0 & 400 & 800 & 1200 & 1600 \\ 10^2 \times [N_2O_5]/molL^{-1} & 1\cdot63 & 1\cdot36 & 1\cdot14 & 0\cdot93 & 0\cdot78 \end{cases}$$

(i) Plot "[N_(2)O_(5)]" against time.",,,,"

(ii) Find the half-life period for the reaction.")

("(iii) Draw a graph between "log[N_(2)O_(5)]" and t.",,,,"

(iv) What is rate law ?"

(v) Calculate the rate constant.

(vi) Calculate the half-life period from k and compare it with (ii).

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16. The rate constant for a first order reaction is $60s^{-1}$. How much time will it take to reduce the initial concentrationof the reactant to its $1/16th$ value ?

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17. During nuclear explosion, one of the products is $.^{90} Sr$ with half $-$ life of 28.1years. If $1\mu g$ of $.^{90} Sr$ was absorbed in the bones of a newly born baby instead of calcium, how much of its will remain after 10 years and 60 years if it is not lost metabolically.

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18. For a first order reaction, show that the time required for 99% completion is twice the time required for the completion of 90% of reaction.

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19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

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20. For the decomposition of azoisopropane to hexane and nitrogen at

54

K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rare constant.

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21. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm

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22. The rate constant for the decomposition of N_2O_5 at various temperatures

is given below:

$T/^{\circ}C$	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between ln k and 1/T and calculate the values of A and E_a. Predict the rate constant at 30° and $50^\circ C$.

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23. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} s^{-1}$ at $546K$. If the energy of activation is $179.9 kJmol^{-1}$, what will be the value of pre $-$ exponential factor?

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24. Consider a certain reaction $A \rightarrow$ Products with $k = 2.0 \times 10^{-2} s^{-1}$. Calculate the concentration of A remaining after $100s$ if the initial concentration of A is $1.0 molL^{-1}$.

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25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.00 hr$. What fraction of sample of sucrose remains after $8 hr$?

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26. The decomposition of hydrocarbon follows the equation

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

Calculate E_a.

Watch Video Solution

27. The rate constant for the first order decompoistion of a certain reaction is described by the equation

$$\log k(s^{-1}) = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

(a) What is the energy of activation for the reaction?

(b) At what temperature will its half-life periof be 256 min ?

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28. The decomposition of A into product has value of k as $4.5 \times 10^3 s^{-1}$ at $10^\circ C$ and energy of activation of $60 kJ mol^{-1}$. At what temperature would k be $1.5 \times 10^4 s^{-1}$?

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29. The time required for 10% completion of a first order reaction at $298K$ is equal to that required for its 25% completion at $308K$. If the value of A is $4 \times 10^{10} s^{-1}$, calculate k at $318K$ and E_a.

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30. The rate of a particular reaction doubles when temperature changes from 27° C to $37^\circ C$. Calculate the energy of activation of such a reaction.

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (MULTIPLE CHOICE QUESTIONS-1)

1. The role of a catalyst is to change

A. Gibbs energy of reaction

B. enthalpy of reaction

C. activation energy of reaction

D. equilibrium constant

Answer: C

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2. In the presence of a catalyst, the heat evolved or absorbed during the reaction:

A. increases

B. decreases

C. remains unchanged

D. may increase or decrease

Answer: C

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3. Activation energy of a chemical reaction can be determined by

A. determining the rate constant at standard temperature

B. determaining the rate constants at two temperatures

C. determining probability of collision

D. using catalyst

Answer: B

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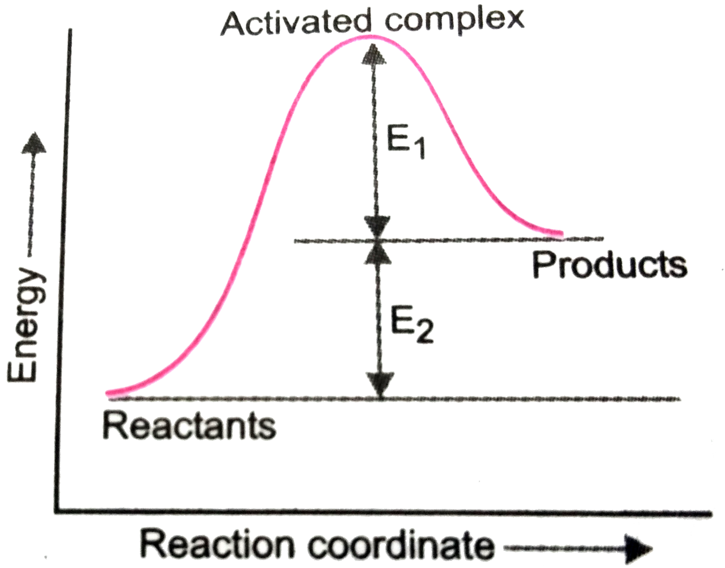
4. Consider Fig. below and mark the correct option.



A. Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

B. Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.

C. Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.

D. Activation energy of backward reaction is E_1 and product is more stable than reactant.

Answer: A

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5. Consider a first order gas phase decomposition reaction given below:

$A(g) \rightarrow B_g + C_g$

The initial pressure of the system before decomposition of A was p_i. After lapse of time t'. Total pressure of the system increased by x units and became P_t. the rate constant k for the reaction is given as

A. $k = \dfrac{2.303}{t} \log \dfrac{P_i}{P_i - x}$

B. $k = \dfrac{2.303}{t} \log \dfrac{P_i}{2P_i - P_t}$

C. $k = \dfrac{2.303}{t} \log \dfrac{P_i}{2P_i + P_t}$

D. $k = \dfrac{2.303}{t} \log \dfrac{P_i}{P_i + x}$

Answer: B

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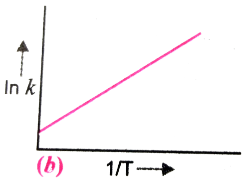
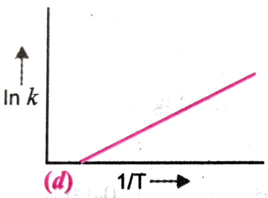
6. According to Arrhenius equation rate constant K is equal to A $e.^{-E_a/RT}$. Which of the following options represents the graph of ln K vs $\frac{1}{T}$?

A.

B. 

C.

D. 

Answer: A

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7. Consider the Arrhenius equation given below and mark the correct option.

$k = Ae^{-\frac{Ea}{RT}}$

A. Rate constant increases exponentially with increasing activation energy and decreasing temperature

B. Rate constant decreases exponentially with increasing activation energy and decreasing temperrature

C. Rate constant increases exponentially with decreasing activation energy and decreasing temperature

D. Rate constant increases exponentially with decreasing activation energy and increasing temperature

Answer: D

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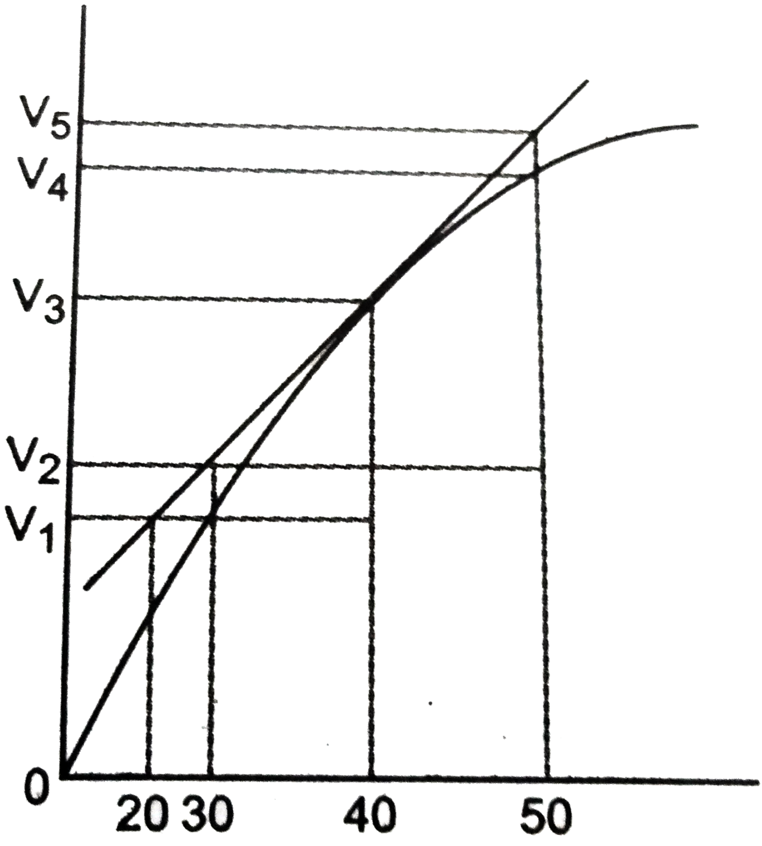
8. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in Fig. below. On the basis of this, mark the correct option.



A. Average rate uptto 40s is $\frac{V_3 - V_2}{40}$

B. Average rate upto 40 seconds is $\frac{V_3 - V_2}{40 - 30}$

C. Average rate upto 40 seconds is $\frac{V_3}{40}$

D. Average rate up to 40 seconds is $\frac{V_3 - V_1}{40 - 20}$

Answer: C

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9. Which of the following statement is not correct about order of a reaction ?

A. The order of a reaction can be a fractional number.

B. Order of a reaction is experimentally determined quantity.

C. The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.

D. The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

Answer: C

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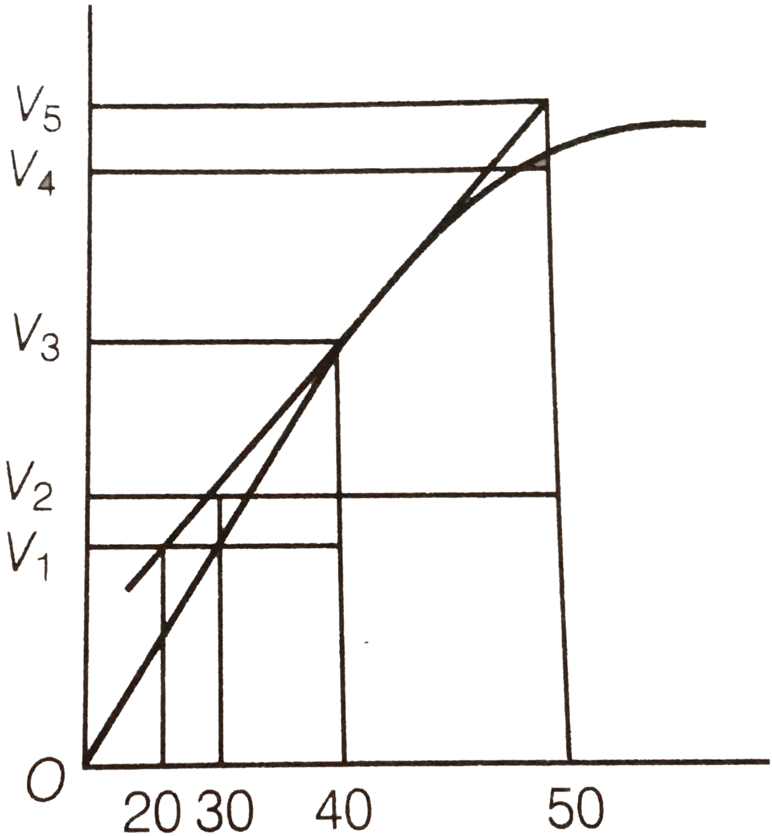
10. Consider the graph given in figure . Which of the following options does not show instantaneous rate of reaction at 40 ?



A. $\frac{V_5 - V_2}{50 - 30}$

B. $\frac{V_4 - V_2}{50 - 30}$

C. $\frac{V_3 - V_2}{40 - 30}$

D. $\frac{V_3 - V_1}{40 - 20}$

Answer: B

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11. Which of the following statements is correct ?

A. The rate of a reaction decreases with passage of time as the concentration of reactants decreases

B. The rate of a reaction is same at any time during the reaction

C. The rate of a reaction is independent of temperature change

D. The rate of a reaction decreases with increase in concentration of reactant (s)

Answer: A

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12. Which of the following expression is correct for the rate of reaction given below ?

$5Br^{-}(aq) + BrO_3^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$.

A. $\dfrac{\Delta[Br^{-}]}{\Delta t} = 5\dfrac{\Delta[H^{+}]}{\Delta t}$

B. $\dfrac{D[Br^{-}]}{\Delta t} = \dfrac{6}{5}\dfrac{\Delta[H^{+}]}{\Delta t}$

C. $\dfrac{D[Br^{-}]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^{+}]}{\Delta t}$

D. $\dfrac{D[Br^{-}]}{\Delta t} = 6\dfrac{\Delta[H^{+}]}{\Delta t}$

Answer: C

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13. Which of the following graphs represents exothermic reaction ?

A. (i) only

B. (ii) only

C. (iii) only

D. (i) and (ii)

Answer: A

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14. Rate law for the reaction, $A + 2B \rightarrow C$ is found to be

Rate $= k[A][B]$

Concentration of reactant 'B' is doubled keeping the concentration of 'A' constant, the value of rate constant will be ______

A. the same

B. doubled

C. quadrupled

D. halved

Answer: A

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15. Which of the following statements is incorrect about the collision theory of chemical reaction?

A. It consider reacting molecules or atoms to be hard spheres and ignores their structural features

B. Number of effective collisions determines the rate of reaction

C. Collision of atoms or molecules possessing sufficient threshold energy results into the product formation

D. Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

Answer: C

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16. A first order reaction is 50% completed in 1.26×10^{14}s. How much time would it take for 100% completion?

A. $1.26 \times 10^{15} s$

B. $2.52 \times 10^{14} s$

C. $2.52 \times 10^{28} s$

D. infinite

Answer: D

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17. Compounds 'A' and 'B' react according to the following chemical equation :

$A(g) + 2 \ \mathrm{B}(g) \rightarrow 2C(g)$

Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Exp.	Initial concentration of [A]/mol L^{-1}	Initial concentration of [B]/mol L^{-1}	Initial rate of formation of [C]/mol L^{-1} s^{-1}
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

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

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

C. Rate $- k[A][B]$

D. Rate $= k[A]^2[B]^0$

Answer: B

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18. Which of the following statement is not correct for the catalyst ?

A. It catalyses the forward and backward reaction to the same extent

B. It alters ΔG of the reaction

C. It is a substance that does not change the equilibrium constant of a reaction

D. It provides an alternate mechanism by reducing activation energy between reactants and products.

Answer: B

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19. The value of rate constant of a pseudo first order reaction

A. depends on the concentration of reactants present in small amount

B. depends on the concentration of reactants

C. is independent of the concentration of reactants

D. depends only on temperature.

Answer: B

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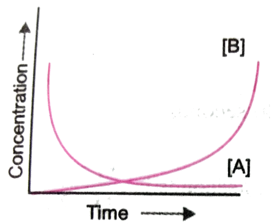
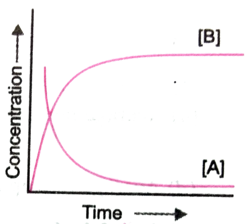
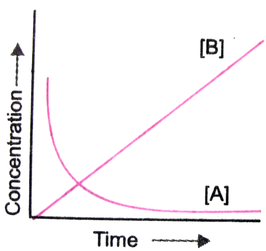
20. Consider the reaction $A \rightarrow B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figure correctly describes the change in concentration of reactants and products with time ?

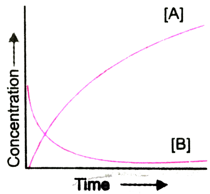
A. 

(a)

B. 

C. 

(c)

D. 

Answer: B

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (MULTIPLE CHOICE QUESTIONS-II)

1. Rate law cannot be determined form balanced chemical equation if â€¦â€¦.. .

A. reverse reaction is involved

B. it is an elementary reaction

C. it is a sequence of elementary reactions

D. any of the reactants is in excess.

Answer: A::C::D

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2. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction ?

A. Order is same as molecularity

B. Order is less than the molecularity

C. Order is grater than the molecularity

D. Molecularity can never be zero.

Answer: A::D

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3. In any unimolecular reaction

A. only one reacting species is involved in the rate determining step

B. the order and the molecularity of slowest step are equal to one

C. the molecularity of the reaction is one and order is zero

D. both molecularity and order of the reaction are one.

Answer: A::B

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4. For a complex reaction â€¦â€¦â€¦ .

A. order of overall reaction is same as molecularity of the slowest step

B. order of overall reaction is less than the molecularity of the slowest step

C. order of overall reaction is greater than molecularity of the slowest step

D. molecularity of the slowest step is never zero or non integer.

Answer: A::D

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5. At high pressure the following reaction is zero order.

$$2NH_3(g) \xrightarrow[\text{Platinum catalyst}]{1130K} N_2(g) + 3H_2(g)$$

Which of the following options are correct for this reaction ?

A. Rate of reaction = Rate constant

B. Rate of the reaction depends on concentration of ammonia

C. Rate of decomposition of ammonia will remain constant until ammonia disappears completely

D. Further increase in pressure will change the rate of reaction.

Answer: A::C::D

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6. During decomposition of an activated complex

A. energy is always released

B. energy is always absorbed

C. energy does not change

D. reactants may be formed

Answer: A::D

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7. According to Maxwell Boltzmann distribution of energy

A. the fraction of molecules with most probable kinetic energy decreases at higher temperatures

B. the fraction of molecules with most probable kinetic energy increases at higher temperatures

C. most probable kinetic energy increases at higher temperatures

D. most probable kinetic energy decreases at higher temperatures.

Answer: A::C

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8. In the graph showing Maxwell Boltzmann distribution of energy ....

.

A. area under the curve must not change with increase in temperature

B. area under the curve increases with increases in temperature

C. area under the curve decreases with increase in temperature

D. with increase in temperature curve broadens and shifts to the right hand side.

Answer: A::D

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9. Which of the following statements are in accordance with the Arrhenius equation?

A. Rate of a reaction increases with increase in temperature

B. Rate of a reaction increases with decrease in activation energy

C. Rate constant decreases exponentially with increase in temperature

D. Rate of reaction decreases with decrease in activation energy.

Answer: A::B

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10. Mark the incorrect statements.

A. Catalyst provides an alternative pathway to reaction mechanism

B. Catalyst raises the activation energy

C. Catalyst lowers the activation energy

D. Catalyst alters enthalpy change of the reaction.

Answer: B::D

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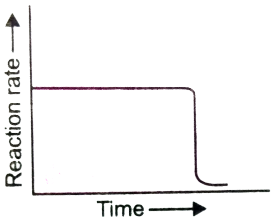
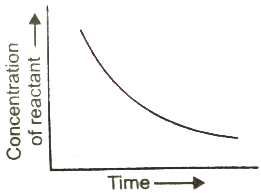
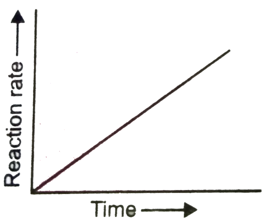
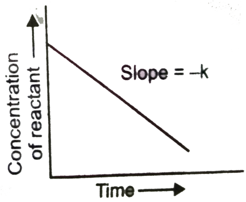
11. Which of the following graphs is correct for a zero order reaction ?

A. 

B. 

C. 

D. 

Answer: A::D

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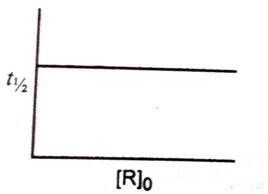
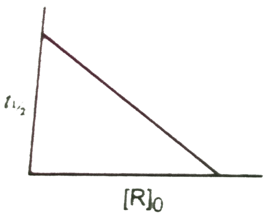
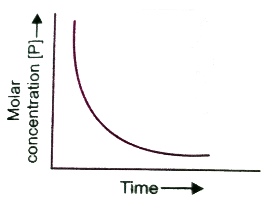
12. Which of the following graph is correct for a first order reaction ?

A. 

B. 

C. 

D.

Answer: A::D

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (SHORT ANSWER QUESTIONS)

1. State a condition under which a bimolecular reaction is kinetically first order reaction.

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2. Write the rate equation for the reaction $2A + B \rightarrow C$ if the order of the reaction is zero.

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3. How can you determine the rate law of the following reactions?

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

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4. For which type of reactions, order and molecularity have the same value?

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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 reaction?

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6. Derive an expression to calculate time required for completion of zero order reaction.

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7. For a reaction $A + B \rightarrow$ Products, the rate law is -Rate $= k[A][B]^{3/2}$

Can the reaction be an elementray reaction ? Explain.

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8. For a certain reaction a large fraction of molecules has energy more than the threshold energy, still the rate of reaction is very slow. The possible reason for this could be that

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9. For a zero order reaction will the molecularity be equal to zero ? Explain.

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10. For a general reaction $A \rightarrow B$, plot of concentration of A vs time is given in Fig. Answer the following questions on the basis of this graph.

(i) What is the order of the reaction ? (ii) What is the slope of the curve ?

(iii) What are the units of rate constant ?

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11. The reaction between $H_2(g)$ and O_2 (g) is highly feasible, yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain.

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12. Â Why does the rate of a reaction increase with rise in temperature?

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13. Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

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14. Why is the probablity of reaction with molecularity higher than three very rare?

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15. Why does the rate of any reaction generally decreases during the course of the reaction?

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16. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example.

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17. Why in the redox titration of $KMnO_4$ vs oxalic acid, we heat oxalic acid solution before starting the titration?

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18. Why can't molecularity of any reaction be equal to zero?

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19. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

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20. Why can we not determine the order of a rection by taking into consideration the balanced chemical equation ?

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (MATCHING TYPE QUESTIONS)

1. Match the statements given in Column I and Column II

	Column I		Column I
(i)	Catalyst alters the rate of reaction	(a)	cannot be
(ii)	Molecularity	(b)	proper or
(iii)	second half life of first order reaction	(c)	by loweri
(iv)	$e^{-E_a/RT}$	(d)	is same a
(v)	Energetically favourable reactions are sometimes slow	(e)	total prol
(vi)	Area under the Maxwell Boltzmann curve is constant	(f)	refers to equal to c

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2. Match the items of Column I and Column II.

	Column I		Column II
(i)	Diamond	(a)	short interval of time
(ii)	Instantaneous rate	(b)	ordinarily rate of conversion is imperceptible
(iii)	Average rate	(c)	long duration of time

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3. Match the items of Column I and Column II.

	Column I	
(i)	Mathematical expression for rate of reaction	(a)
(ii)	Rate of reaction for zero order reaction is equal to	(b)
(iii)	Units of rate constant for zero order reaction is same as that of	(c)
(iv)	Order of a complex reaction is determined by	(d)

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (ASSERTION AND REASON TYPE QUESTIONS)

1. Assertion: Order of the reaction can be zero or fractional.

Reason: We cannot determine order from balanced chemical equation.

A. Both assertion and reason are correct and the reason is correct explananation of assertion.

B. Both assertion and reason are correct but reason does not explain assertion.

C. Assertion is correct but reason is incorrect.

D. Both assertion and reason are incorrect.

Answer: B

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (ASSERTION AND REASON TYPE OUESTIONS)

1. Assertion (A) Order and molecularity are same.

Reason (R) Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

A. Both assertion and reason are correct and the reason is correct explananation of assertion.

B. Both assertion and reason are correct but reason does not explain assertion.

C. Assertion is correct but reason is incorrect.

D. Assertion is incorrect but reason is correct.

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2. Assertion (A) The enthalpy of reaction remains constant in the presence of a catalyst.

Reason (R) A catalyst participating in the reaction froms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

A. Both assertion and reason are correct and the reason is correct explananation of assertion.

B. Both assertion and reason are correct but reason does not explain assertion.

C. Assertion is correct but reason is incorrect.

D. Both assertion and reason are incorrect.

Answer: A

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3. Assertion: All collisions of reactant molecules lead to product formation.

Reason: Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formations.

A. Both assertion and reason are correct and the reason is correct explananation of assertion.

B. Both assertion and reason are correct but reason does not explain assertion.

C. Assertion is correct but reason is incorrect.

D. Assertion is incorrect but reason is correct.

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4. Assertion (A) Rate constant determined form Arrhenius equations are fairly accurate for simple as well as complex molecules.

Reason (R) Reatant molecules undergo chemical irrespective of their orientation during collison.

A. Both assertion and reason are correct and the reason is correct explananation of assertion.

B. Both assertion and reason are correct but reason does not explain assertion.

C. Assertion is correct but reason is incorrect.

D. Both assertion and reason are incorrect.

Answer: C

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTTIONS (LONG ANSWER QUESTIONS)

1. All energetically effective collisions do not result in a chemical change. Explain with the help of an example.

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2. What happens to most probable kinetic energy and the energy of activation with increases in temperature?

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3. Describe why the enthalpy of a reaction remains unchanged when a catalyst is used in a reaction.

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4. Explain the difference between instantaneous rate of a reaction and average rate of a reaction .

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5. With the help of an example explain what is meant by pseudo first order reaction .

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) I. General introduction and rates of reactions

1. Write expression for rate of reaction in terms of each reactant and product for the reaction

$N_2 + 3H_2 \rightarrow 2NH_3$.

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2. For the straight reaction,

$X_2(g) + 2Y_2(g) \rightarrow 2 \ \mathrm{XY}_2(g)$, write the rate equation in terms of disappearance of Y_2

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3. The rate law for the following reactions:

$Ester + H^{\oplus} \rightarrow \mathrm{Acid} + \mathrm{Alcohol}$, is

$dx/dt = k(ester)\left[H_3O^{\oplus}\right]^0$

What would be the effect on the rate if

(a) concentration of ester is doubled.

(b) concentration of $H^{\oplus}$ ion is doubled.

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4. Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction

$3 \ H_2(g) + N_2(g) \rightarrow 2 \ NH_3(g)$

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5. For the reaction $N_2(g) + 3 \ H_2(g) \rightarrow 2 \ NH_3(g)$, if $\Delta[NH_3] / \Delta t = 4 \times 10^{-8} \ \text{mol L}^{-1} s^{-1}$ what is the value of $-\Delta[H_2] / \Delta t$?

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6. Write the names of four factors affecting the rate of a reaction.

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) II. Rate law, order of reaction, rate constant and its units

1. Define rate of reaction and rate constant.

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2. Define rate of reaction and rate constant.

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3. What is the difference between Rate law and Law of Mass Action ?

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4. Give an example of a reaction having fractional order.

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5. The rate law for decomposition N_2O_5 is rate $=k[N_2O_5]$

What is the significance of k in the equation?

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6. Define the term 'order of reaction' for chemical reactions.

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7. Give one example of first order reaction.

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8. Rate of reaction is given by the eqution : Rate = $k[A]^2[B]$. What are the units for the rate and rate constant for the reaction?

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9. The decomposittion reaction of ammonia gas on platinum surface has a rate constant $= 2.5 \times 10^{-4} \text{ mol L}^{-1} s^{-1}$. What is the order of the reaction ?

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10. The rate constant of a reaction is $3 \times 10^{2} \text{ min}^{-1}$. What is the order of reaction ?

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) III. Molecularity, mechanism and difference between order and molecularity

1. Define molecularity of a reaction.

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2. Give one example of a reaction where order and molecularity are equal.

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3. What is the rate determining step of a reaction ?

Watch Video Solution

4. What is meant by an elementary reaction ?

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5. What is the molecularity of the reaction, $Cl \rightarrow \frac{1}{2}Cl_2(g)$?

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6. For the reaction $NO_2 + CO \to CO_2 + NO$, the rate law is : Rate $= k[NO_2]^2$. Propose the probable mechanism of this reaction.

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7. For a reaction : $A + H_2O \to B$, $\text{Rate} \propto A]$. What is its (i) Molecularity (ii) Order of reaction ?

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8. State one condition under which a bimolecular reaction may be kinetically of first order reactions.

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) IV. Integrated rate equations, half-life, determination of rate law, rate const. and order

1. In the reaction $aA + bB \rightarrow$ products, if concentration of A is doubled (keeping B constant) the initial rate becomes four times and if B is doubled (keeping A constant), the rate becomes double. What is the rate law equation and order of reaction ?

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2. The reaction A+B $\rightarrow$ C. has zero order. What is the rate equation?

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3. A substance with initial concentration 'a' follows zero order kinetics. In how much time, will the reactions go to completion ?

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4. Give an example of a zero order reaction and write an expression for its rate constant.

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5. Write the expression showing the change of concentration with time in the exponential form for reactions of first order.

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6. How is half-life period $\left(t_{1/2}\right)$ of a first order reaction related to its rate constant (k) ?

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7. How is half-life period of a initial concentration for a second order reaction ?

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8. If half-life period of a reaction is inversely proportional to initial concentration of the reactant, what is the order of reaction ?

A. Zero

B. first

C. Second

D. None of the above

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9. For a reaction $R \rightarrow P$, half -life $(t_{1/2})$ is observed to be independent of the initial concentration of reactants. What is the order of reaction ?

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10. Write expression for half-life in case of a reaction between hydrogen and chlorine to form hydrochloric acid gas.

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11. Three-fourth of a first order reaction is completed in 32 minutes. What is the half-life period of this reaction ?

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12. Draw a schematic graph showing how the rate of first order reaction changes with change in concentration of reactants.

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) V. First order reactions, pseudo first order reactions and radioactive disintegration

1. What is meant by pseudo first order reaction? Given an example of pseudo first order reaction. Write rate equation for the same.

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2. Radioactive disintegration is a first order reaction. Explain why.

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) VI. Activation energy, effect of temp. on rate (Arrhenius eqn.) and effect of catalyst on rate

1. Define activation energy of a reaction.

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2. Define temperature coefficient of a reaction.

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3. The activation energy of a reaction is zero. Will the rate constant of the reaction depend upon temperature ? Give reason.

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4. In Arrhenius equation $k = Ae^{-E_a/RT}\big)$, A is the value of the rate constant

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ADDITIONAL QUESTIONS (VERY SHORT ANSWER QUESTIONS) VII. Collision theory

1. What are the two necessary conditions for a collision between two molecules to be effective ?

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) I. General introduction and rates of reactions

1. What is meant by reaction rate ? Give its symbolic expression expression and units for the reaction

$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$

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2. Differentiate between :Average rate and instantaneous rate of a chemical reaction.

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3. Express the relationship between the rate of production of HCl and the rate of disappearance of H_2 in the reaction : $H_2 + Cl_2 \rightarrow 2HCl$

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) II. Rate law, order of reaction, rate constant and its units

1. Define the following :

(i) Order of a reaction (ii) Molecularity of a reaction (iii) Rate law (iv) Law of mass action

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2. What is meant by the 'rate constant, k' of a reaction ? If the concentration be expressed in mol L^{-1} units and time in seconds, what would be the units for k (i) for a zero order reaction and (ii) for a first order reaction?

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3. What is order of reaction ? Write units of the rate constant k for zero order, first order and second order reaction.

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4. The decomposition of dimethyl ether leads to the formation of $CH_4, H_2,$ and CO and the reaction rate is given by

Rate $= k[CH_3OCH_3]^{3/2}$

The rate of reaction is followed by increase in the pressure in a closed vessel , so the rate can also be expressed in terms of the partial pressure of dimethyl either, $i.e.$,

Rate $= k[p_{CH_3OCH_3}]^{3/2}$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant ?

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5. Write any four differences between 'rate of reaction' and 'rate constant' of a reaction.

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) III. Molecularity, mechanism and difference between order and molecularity

1. Comment on the statement that molecularity of the slowest step in a reaction gives the overall molecularity of the reaction.

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2. What is the rate determining step of a reaction ?

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3. The rate expressions of some reactions are given below :

(a) $2N_2O_5 \rightarrow 4NO_2 + O_2, \quad \text{Rate} \quad = k[N_2O_5]$

(b) $2NO_2 + F_2 \rightarrow 2NO_2F, \quad \text{Rate} \quad = k[NO_2][F_2]$

(c) $NO_2 + CO \rightarrow CO_2 + NO, \quad \text{Rate} \quad = k[NO_2]^2$

Propose the probable mechanism of each of the above reactions.

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4. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide :

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

The rate law for this reaction is : Rate $= k[NO]^2[O_2]$.

Propose a mechanism for the above reaction.

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5. Give any four differences between order of a reaction and its molecularity ?

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

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7. Define and explain the term 'molecularity of a reaction' with suitable example.

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) IV. Integrated rate equations, half-life, determination of rate law, rate const, and order

1. Derive the relationship between rate constant and half-life period of a first order reaction.

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2. Show that for the reactions of first order (i) Half-life period is independent of initial concentrations.

(ii) Units of rate constant do not depend upon the units of concentration.

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3. Derive the equation for the rate constant of a first order reaction and show that the time required for the completion of half of the first order reaction is independent of initial concentration.

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4. Rate of reaction is the change in concentration of any one of the reactants or any one of the products in unit time

(i) Express the rate of the following reaction in terms of reactants and products :

$2\ \text{HI} \rightarrow H_2 + I_2$

(ii) If the expression for the above reaction is, rate $= k[HI]^2$, what is the order of the reaction.

(iii) Are the order and molecularity of the above reaction same ? Give reason.

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5. Derive integrated rate equation for rate constant for a first order reactants. What would be units of the first order rate constant, if the concentration is expressed in moles per litre and time in seconds ?

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6. (a) How does the rate of reaction depend upon the concentration of reactants ?

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7. (b) What is rate constant ? Write 'two applications' of rate law.

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8. Define half-life period. How is it related to the order of a reaction ?

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) V. First order reactions, pseudo first order reactions and reactions and radioactive disintegration

1. What are Pseudounimolecular reactions ? Explain with the help of a suitable example.

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2. The hydrolysis of ethyl acetate $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$ is a reaction of

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3. What do you mean by molecularity and order of a reaction ? Explain why their values are different in the reaction : $CH_3COOC_2H_5 + H_2O \to CH_3COOH + C_2H_5OH$.

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4. Define half-life period and average life. Derive relation between them.

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5. For the reaction $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$, write

(i) Rate of reaction expression (ii) rate law equation (iii) molecularity (iv) order of reaction

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) VI. Activation energy, effect of temp. on rate (Arrhenius eqn.) and effect of catalyst on rate

1. Define the term Activation energy. Why different reactions proceed at different speeds ?

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2. Define energy of activation. Draw diagram of energy profile to show the influence of a positive catalyst on the energy of activation of a reaction.

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3. The reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ is feasible. How is that hydrogen and oxygen mixture allowed to stand at room temperature shows no formation of water at all ?

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

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

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6. Write Arrhenius equation showing the effect of temperature on the reaction rate. What do different symbols signify ? How does it help in the calculation of activation energy of a reaction ?

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7. What is activation energy ? How is the rate constant of a reaction related to its activation energy ?

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8. How is rate constant of a reaction affected by temperature ? Write the name of this relation. How will you calculate activation energy of a reaction with the help of this relation ?

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9. Briefly explain the effect of adding catalyst on the rate of a reaction.

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) VII. Collision theory

1. Write a short note on 'collision theory of reaction rates'.

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ADDITIONAL QUESTIONS (SHORT ANSWER QUESTIONS) VIII. Miscellaneous

1. Explain : (i) One gram of pulverised wood burns faster than a one gram piece of wood.

(ii) An increase of 10 K in temperature rarely doubles the kinetic energy of particles but this increase in temperature may be enough to double the rate of reaction.

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2. Explain the effect of (a) Concentration of the reactants (b) Presence of a catalyst on the rate of a chemical reaction.

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3. Define the following terms : (i) Collision frequency

(ii) Half-life period of a reaction.

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4. Define the following terms : (i) Order of reaction

(ii) Threshold energy.

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5. Write short notes on :

(i) Activation energy (ii) Arrhenius equation.

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ADDITIONAL QUESTIONS (LONG ANSWER QUESTIONS)

1. (a) Derive the general form of the expression for the half-life of first order reaction.

(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$?

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2. (a) List the factors on which the rate of a chemical reaction depends.

(b) The half-life for the decay of radioactive ^{14}C is 5730 years. An archaeological artifact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artifact.

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3. (a) Explain the following terms : (i) Rate of a reaction. (ii) Activation energy of a reaction.

(b) The decomposition of phosphine, PH_3, proceeds according to the following equation :

$4\ \mathrm{PH}_3(g) \rightarrow P_4(g) + 6\ \mathrm{H}_2(g)$

It is found that the reaction follows the following rate equation :

Rate $= k[PH_3]$

The half-life of PH_3 is 37.9 s at $120^\circ C$.

(i) How much time is required for $3/4th$ of PH_3 to decompose.

(ii) What fractional of the original sample of PH_3 remains behind after 1 minute ?

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4. (a) Illustrate graphically the effect of catalyst on activation energy.

(b) Catalysts have no effect on the equilibrium constant. Why ?

(c) The decomposition of A into product has value of k as $4.5 \times 10^3 s^{-1}$ at $10^\circ C$ and activation energy is 60 kJ mol^{-1}. Calculate the temperature at which the value of k will be $1.5 \times 10^4 s^{-1}$.

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5. (a) Rate constant of a chemical reaction rises to double by increase in temperature of $10^\circ C$. Explain with labelled distribution curve.

(b) The rate constant of a first order reaction increases by four times when the temperature changes from 350 K to 400 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature $\left(R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}, \log 4 = 0.6021\right)$

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6. (a) The rate of reaction increases in presence of catalyst. Explain the statement by plotting a curve between reaction coordinate and energy.

(b) For a reaction, the initial concentration of reactant is 0.4 M and rate constant is $2.5 \times 10^{-4} \text{mol L}^{-1} s^{-1}$. Calculate the half-life period of the reaction.

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7. Describe the experiment to determine the effect of temperature on the rate of reaction between potassium persulphate and potassium iodide.

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8. Define order of a reaction and molecularity of reaction. Drive a general expression for specific rate constant of first order reaction.

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9. (a) A reaction is second order in A and first order in B .

(I Write the differential rate equation.

(ii) How is the rate afected on increasing the concentration of A three times?

(iii) How is the rate affected when the concentration of both A and B doubled?

(b) A first order reaction takes 40 minutes for 30% decomposition. Calculate t_(1//2)` for this reaction. (Given log 1.428 = 0.1548)

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10. (a) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

(b) Rate constant 'K' of a reaction varies with temperature 'T' according to the equation : $\log K = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$

Where E_a is the activation energy. When a graph is plotted for log k Vs $\frac{1}{T}$ a straight line with a slope of -4250 K is obtained. Calculate E_a for the reaction.

$(R = 8.314 JK^{-1} mol^{-1})$

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11. (a) Discuss the difference between order and molecularity of a chemical reaction.

(b) Discuss the concept of activation energy in a chemical reaction and explain the relation between reaction rate and temperature.

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12. For the hydrolysis of methyl acetate in aqueous solution the following results were obtained :

(i) Show that it follows pseudo first order reaction as the concentration of water remains constant.

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

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13. (a) For a reaction $A + B \to P$, the rate is given by Rate $= k[A][B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled ?

(ii) What is the overall order of reaction if A is present in large excess ?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90%. Completion of this reaction $(\log 2 = 0.310)$.

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HIGHER ORDER THINKING SKILLS (QUESTIONS AND PROBLEMS WITH ANSWERS/SOLUTIONS) HOTS QUESTIONS

1. The rate of decomposition of ammonia is found to depend upon the concentration of NH_3 according to the equation

$$-\frac{d[NH_3]}{dt} = \frac{k_1[NH_3]}{1 + k_2[NH_3]}$$

What will be the order of reaction when

(i) concentration of NH_3 is very high ? (ii) concentration of NH_3 is very low ?

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2. The rate law equation for the reaction $A \rightarrow B$ is found to be

$$-\frac{d[A]}{dt} = k[A]^{1/2}$$

If $[A]_0$ were the initial concentration of A, derive expressions for

(i) rate constant in the integrated form (ii) half-life period of the reaction

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3. While studying the decompoistion of gaseous N_2O_5, it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained form this observation?

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4. Write the elementary steps of the reaction $2 \ O_3 \Leftrightarrow 3 \ O_2$ and hence derive the rate law expression for this reaction. Comment on the order of reaction.

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5. For a first order reaction, derive expression for the degree of dissociation of the reactant in the exponential form.

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6. For a general nth order reaction $A \rightarrow P$ with initial concentration of the reactant 'a' and rate constant 'k', derive expression for time for 75% completion of the reaction in terms of a, n and k.

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7. The rate of change of concentration of (A) for reaction $A \rightarrow B$ is given by

$$-\frac{d[A]}{dt} = k[A]^{1/3}$$

Derive expression for half-life period of the reaction.

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HIGHER ORDER THINKING SKILLS (QUESTIONS AND PROBLEMS WITH ANSWERS/SOLUTIONS) HOTS PROBLEMS

1. The half time of first order decomposition of nitramide is 2.1 hour at $15^{\circ} C$.

$$NH_2NO_{2(aq.)} \rightarrow N_2O_{(g)} + H_2O_{(l)}$$

If $6.2g$ of NH_2NO_2 is allowed to decompose, calculate:

(i) Time taken for NH_2NO_2 is decompose 99%.

(ii) Volume of dry N_2O produced at this point measured at STP.

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2. The time required for 10% completion of a first order reaction at $298K$ is equal to that required for its 25% completion at $308K$. If the pre-exponential factor for the reaction is $3.56 \times 10^9 s^{-1}$, calculate its rate constant at $318K$ and also the energy of activation.

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3. For the reaction, $N_2O_5(g) = 2\ \mathrm{NO}_2(g) + 0.5\ \mathrm{O}_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

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4. $2X(g) \rightarrow 3Y(g) + 2Z(g)$

Time (in min)	0	100	200
Partial pressure of X (mm Hg)	800	400	200

Assuming ideal gas condition, calculate

(a) Order of reaction

(b) Rate constant

(c) Time taken for 75% completion of reaction

(d) Total pressure when $p_x = 700mm$

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5. The values of the rate constant for the decomposition of HI into H_2 and I_2 at different temperatures are given below :

T/K	633	667	710	738
$10^4 k / M^{-1}s^{-1}$	0.19	1.00	8.31	25.1

Draw a graph between ln k against $1/T$ and calculate the values of Arrhenius parameters.

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6. Two first order reactions proceed at the same rate at $25^\circ C$ when started with same initial concentration. The temperature coefficient of the first reaction is 2 while that of the second reaction is 3. What will be the ratio of the rates reactions at $55^\circ C$?

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7. When inversion of sucrose is studied at pH = 5, the half-life period is always found to be 500 minutes irrespective of any initial concentration but when it is studied at pH = 6, the half-life period is found to be 50 minutes. Derive the rate law expression for the inversion of sucrose.

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8. The inactivation of a viral preparation in a chemical bath is found to be first order reaction. If in the beginning, 2.5% of the virus is inactivated per minute, calculate the rate constant of the viral inactivation.

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9. For a consecutive reaction $R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3$, if initial concentration of R_1 is 100 M and $k_1 : k_2 = 1 : 0.15$, calculate the value of $t_{\max}\left(\text{Given } k_1 = 4.0 \times 10^{-2} \text{min}^{-1}\right)$.

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10. A given sample of milk turns sour at room temperature $(27^{\circ} C)$ in five hours. In a refrigerator at $-3^{\circ} C$, it can be stored 10 times longer. The energy of acrivation for the souring of milk is

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11. The concentration of an organic compound in chloroform is $6.15 \text{ g per } 100 \text{ mL}$ of the solution. A portion of this solution in a 5 cm polarimeter tube causes an observed rotation of -1.2°. What is the specific rotation of the compound ?

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VALUE BASED QUESTIONS (WITH ANSWERS)

1. Manish went to market to buy fruit and vegetables. He was attracted to buy fruit and vegetables which were big in size. When he reached home, his mother told him that he had not brought good quality stuff. She explained to him that these had been grown to this size by using synthetic fertilizers and pesticides which are harmful for our health.

After reading the above paragraph, answer the following questions :

(i) What values have been expressed in the above paragraph ?

(ii) How and why fertilizers and pesticides are harmful to human health. What solution do you suggest to the problem ?

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2. While walking on the footpath, sometimes some autos pass on road which exhaust a lot of smoke and gases causing pollution and we feel suffocated. Meenu discussed the problem with her teacher as to why these vehicles caused pollution. The teacher explained to her that exhaust pipes of some vehicles are not fitted with good quality catalytic convertors or people don't get the service of their vehicle done at regular times.

New, answer the following questions :

(i) What values are expressed in the above paragraph ?

(ii) How catalytic convertors fitted in the exhaust pipe help in reducing pollution ?

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (I. Multiple Choice Questions)

1. In a catalytic experiment involving Haber's process, $N_2(g) + 3\ \mathrm{H}_2(g) \rightarrow 2\ \mathrm{NH}_3(g)$, the rate of reaction was measured as : Rate $= \dfrac{d[NH_3]}{dt} = 2.0 \times 10^{-4} \mathrm{M\,s}^{-1}$. If there were no side reactions, what was the rate of reaction expressed in terms of N_2 ?

A. $1 \times 10^{-4} \mathrm{M\,s}^{-1}$

B. $4 \times 10^{-4} \mathrm{M\,s}^{-1}$

C. $5 \times 10^{-3} \mathrm{M\,s}^{-1}$

D. $1 \times 10^{-3} \mathrm{M\,s}^{-1}$

Answer: A

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2. The decomposition of N_2O_5 in CCl_4 at 318 K is studied by monitoring the concentration of N_2O_5 in the solution. Initially, the concentration of N_2O_5 is $2.4 \ \mathrm{mol\,L}^{-1}$ and after 200 minutes, it is reduced to $2.00 \ \mathrm{mol\,L}^{-1}$. What is the rate of production of NO_2 during this period in $molL$^(-1) $\min^{-1}$?

A. 4×10^{-3}

B. 2×10^{-3}

C. 1×10^{-3}

D. 2×10^{-4}

Answer: A

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3. In the synthesis of ammonia from nitrogen and hydrogen gases, if 6×10^{-2} mole of hydrogen disappears in 10 minutes, the number of moles of ammonia formed in 0.3 minutes is

A. 1.8×10^{-2}

B. 1.2×10^{-3}

C. 4×10^{-2}

D. 3.6×10^{-2}

Answer: B

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4. 100 cm^3 of 1 M CH_3COOH was mixed with 100 cm^3 of 2 M CH_3OH to form an ester. The change in the initial rate if each solution is diluted with equal volume of water would be

A. 4 times

B. 0.25 times

C. 2 times

D. 0.5 times

Answer: B

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5. The rate of a gaseous reaction is generally expressed in terms of $\frac{dP}{dt}$. If it were expressed in terms of change in number of moles per unit time $\left(\frac{dn}{dt}\right)$ or in terms of change in molar concentration per unit time $\left(\frac{dC}{dt}\right)$, which of the following relationship will hold good ?

A. $\frac{dC}{dt}=\frac{dn}{dt}=\frac{dP}{dt}$

B. $\frac{dC}{dt}=\frac{1}{V}\left(\frac{dn}{dt}\right)=\frac{1}{RT}\left(\frac{dP}{dt}\right)$

C. $\frac{dC}{dt}=\frac{dn}{dt}=\frac{V}{RT}\left(\frac{dP}{dt}\right)$

D. None of these

Answer: B

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6. In a reversible reaction $2NO_2 \underset{k_2}{\overset{k_1}{\Longleftrightarrow}} N_2O_4$, the rate of disappearance of NO_2 is equal to

A. $\frac{2k_1}{k_2}[NO_2]^2$

B. $2\ \mathrm{k}_1[NO_2]^2 - 2\ \mathrm{k}_2[N_2O_4]$

C. $2\ \mathrm{k}_1[NO_2]^2 - k_2[N_2O_4]$

D. $(2\ \mathrm{k}_1 - k_2)[NO_2]$

Answer: B

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7. The rate law for a reaction between the substances A and B is given by

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

On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as:

A. $m+n$

B. $(n-m)$

C. 2^{n-m}

D. $\frac{1}{2^{(m+n)}}$

Answer: C

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8. Consider the decomposition of N_2O_5 as

$N_2O_5 \rightarrow 2NO_2 + 1/2O_2$

The rate of reaction is given by

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt}$$

$$= k_1[N_2O_5]$$

Therefore $\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5]$

$$\frac{+d[NO_2]}{dt} = 2k_1[N_2O_5] = k_1[N_2O_5]$$

$$\frac{+d[O_2]}{dt} = \frac{1}{2}k_1[N_2O_5] = k_1[N_2O_5]$$

Choose the correct option

A. $k_1 = k_1' = k_1''$

B. $k_1 = 2\ \mathrm{k}_1' = k_1''$

C. $2\ \mathrm{k}_1 = k_1' = 4\ \mathrm{k}_1''$

D. $4\ \mathrm{k}_1 = 2\ \mathrm{k}_1' = k_1''$

Answer: C

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9. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one of the following is true for the rate of these reactions if concentration of the reactant is same and greater than 1 M ?

A. $r_1 = r_2 = r_3$

B. $r_1 > r_2 > r_3$

C. $r_1 < r_2 < r_3$

D. There can be no definite order

Answer: C

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10. For the reaction,

$$Ag^+ + 2\ \mathrm{NH_3} \Leftrightarrow \left[\mathrm{Ag}(NH_3)_2\right]^+,$$

the net rate of reaction is given by

$$\frac{dx}{dt} = 2 \times 10^7 \left[\mathrm{Ag}^+\right][NH_3]^2 - 1 \times 10^{-2}\left[\mathrm{Ag}(NH_3)_2\right]^+$$

Then which of the following statement/s is/are correct ?

A. Rate constant for forward reaction $= 2 \times 10^7$

B. Rate constant for backward reaction $= 1 \times 10^{-2}$

C. Equilibrium constant of the reaction $= 2 \times 10^9$

D. All the above

Answer: D

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11. For the reaction $A + B \rightarrow C + D$, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the concentration of only B simply doubles the reaction rate. Find the rate law for the above equation.

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

B. $r = k[A][B]^2$

C. $r = k[A]^2[B]$

D. $r = k[A][B]$

Answer: C

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12. If rate $= k[H^{+}]^{n}$ and it becomes 100 times when the pH changes from 2 to 1, then the order of reaction is

A. 0

B. 1

C. 2

D. 3

Answer: C

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13. A hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below:

$A_2 \Leftrightarrow A + A(\text{fast})$

$A + B_2 \rightarrow AB + B$ (slow)

$A + B \rightarrow AB$ (fast)

The order of the overall reaction is

A. zero

B. 1

C. $1\frac{1}{2}$

D. 2

Answer: C

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14. Higher order (> 3) reaction are rare due to :

A. Low probability of simultaneos collision of all the reacting species

B. Increase in entropy and activation energy as more molecules are involved

C. shifting of equilibrium towards reactants due to elastic collisions

D. loss of active species on collision

Answer: A

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15. Mechanism of a hypothetical reaction

$X_2 + Y_2 \rightarrow 2XY$ is given below:

(i) $X_2 \rightarrow X + X$ (fast)

(ii) $X + Y_2 \Leftrightarrow XY + Y$ (slow)

(iii) $X + Y \rightarrow XY$ (fast)

The overall order of the reaction will be :

A. 1

B. 2

C. 0

D. 1.5

Answer: D

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16. A first order reaction has a specific reaction rate of $10^{-2} s^{-1}$. How much time will it take for 20 g of the reactant to reduce to 5 g ?

A. 238.6 second

B. 138.6 second

C. 346.5 second

D. 693.0 second

Answer: B

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17. The rate of the reaction $A \rightarrow$ products, at the initial concentration of $3.24 \times 10^{-2} M$ is nine times its rate at another initial concentration of $1.2 \times 10^{-3} M$. The order of reaction is

A. $\frac{1}{2}$

B. $\frac{3}{4}$

C. $\frac{3}{2}$

D. $\frac{2}{3}$

Answer: D

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18. The time for half life period of a certain reaction $A \rightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A', is $2.0 \ \text{mol L}^{-1}$, how much time does it take for its concentration to come from 0.50 to $0.25 \ \text{mol L}^{-1}$, how much time does it take for its concentration to come from 0.50 to $0.25 \ \text{mol L}^{-1}$ if it is a zero order reaction ?

A. 0.25 h

B. 1 h

C. 4 h

D. 0.5 h

Answer: A

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19. The rate constant of the reaction $A \rightarrow B$ is 0.6×10^{3} mole per litre per second. If the concentration of A is 5 M, then concentration of B after 20 minutes is

A. $0.36 \quad \mathrm{M}$

B. $0.72 \quad \mathrm{M}$

C. $1.08 \quad \mathrm{M}$

D. $3.60 \quad \mathrm{M}$

Answer: B

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20. The half life of a substance in a certain enzyme catalyzed reaction is 138s. The time required for the concentration of the substance to fall from $1.28mgL^{-1} \rightarrow 0.04mgL^{-1}$:

A. 414 s

B. 552 s

C. 690 s

D. 276 s

Answer: C

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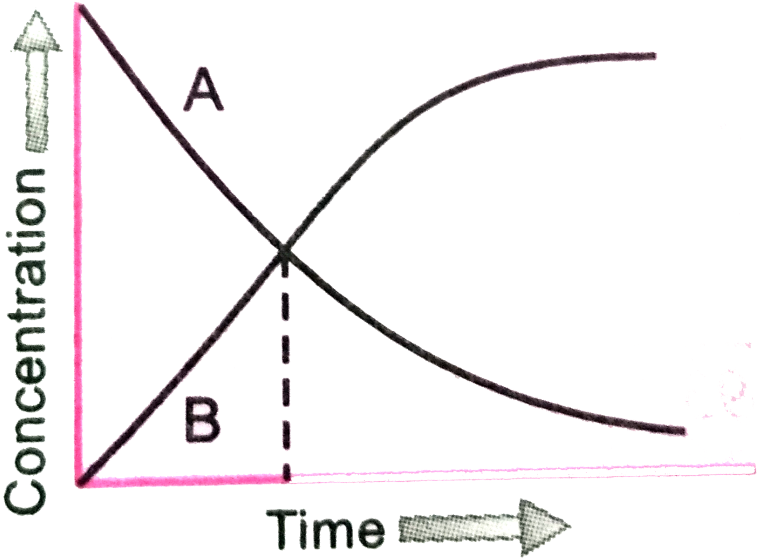
21. The figure below depicts the change in the concentration of the species A and B for the reaction $A \rightarrow B$, as a function of time. The point of intersection of the two curves represents



A. $t_{1/4}$

B. $t_{1/3}$

C. $t_{1/2}$

D. The method cannot be used to predict fractional life time

Answer: C

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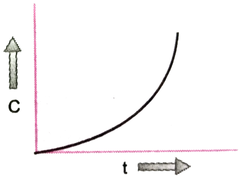
22. The plote between concentration versus time for a zero order reaction is represented by :

A.

B.

C. 

D.

Answer: B

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23. In the reaction,

$P + Q \rightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50% of the reaction of P. The concentration of Q varies with the reaction time as shown in the figure. The overall order of the reaction is

A. 2

B. 3

C. 0

D. 1

Answer: D

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24. A first order reaction is carried out starting with $10 \ \text{mol L}^{-1}$ of the reactant. It is $40\,\%$ complete in one hour. If the same reaction is carried out with an initial concentration of $5 \ \text{mol L}^{-1}$, the percentage of the reaction that is completed in one hour will be

A. $40\,\%$

B. $80\,\%$

C. 20%

D. 60%

Answer: A

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25. Half-lives of a first order and a zero order reaction are same. Then the ratio of the initial rates of the first order reaction to that of zero order reaction is

A. $\frac{1}{0.693}$

B. 2×0.693

C. 0.693

D. $\frac{2}{0.693}$

Answer: B

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26. For a first order reaction, the time taken to reduce the initial concentration by a factor of $\frac{1}{4}$ is 10 minutes. The time required to reduce initial concentration by a factor of $1/16$ will be

A. 20 min

B. 10 min

C. 80 min

D. 40 min

Answer: D

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27. The rate constant of a second order reactions $2A \rightarrow$ Products, is $10^{-4}\text{lit mol}^{-1}\text{min}^{-1}$. The initial concentration of the reactant is $10^{-2}\text{mol lit}^{-1}$. What is the half life (in min) ?

A. 10

B. 1000

C. 100

D. 10^6

Answer: D

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28. The time taken for 10 % completion of a first order reaction is 20 minutes. Then for 19 % completion, the reaction will take

A. 40 mins

B. 60 mins

C. 30 mins

D. 50 mins

Answer: A

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29. The following data is obtained during the first order thermal decomposition of

$2\ \mathrm{A}(g) \rightarrow\ \mathrm{B}(g) +\ \mathrm{C}(s)$

at constant volume and temperature

S. No.	Time	Total pressure in pascals
1.	At the end of 10 minutes	300
2.	After completion	200

The rate constant in $\min^{-1}$ is

A. 0.0693

B. 6.93

C. 0.00693

D. 69.3

Answer: A

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30. Rate constant of a reaction is 0.0693 min^{-1}. Starting with 10 mol L^{-1}, rate of reaction after 10 minutes will be

A. $0.0693 \text{ M min}^{-1}$

B. $0.0693 \times 2.5 \text{ M min}^{-1}$

C. $0.0693 \times 5 \text{ M min}^{-1}$

D. $0.0693 \times 10 \text{ M min}^{-1}$

Answer: C

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31. For the reaction $A + 2B \rightarrow$ C, the reaction rate is doubled if the concentration of A is doubled , the rate is increased by four times when concentrations of both A and B are increased by four times . The order of the reaction is ______.

A. 3

B. 0

C. 1

D. 2

Answer: C

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32. The initial rates of reaction $3A + 2B + C \rightarrow$ products at different initial concentration are given below

Initial rate, MS^{-1}	$\|A_0\|M$	$\|B_0\|M$	$\|C_0\|M$
5.0×10^{-3}	0.010	0.005	0.010
5.0×10^{-3}	0.010	0.005	0.015
1.0×10^{-2}	0.010	0.010	0.010
1.25×10^{-3}	0.005	0.005	0.010

The order of reaction with respect to the reacts A, B and C are respectively.

A. 3, 2, 0

B. 3, 2, 1

C. $2, 2, 0$

D. $2, 1, 0$

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33. At 500 K, the half-life period of a gaseous reaction at the initial pressure of 80 kPa is 350 sec. When the pressure is 40 kPa, the half life period is 175 sec. The order of reaction is

A. zero

B. one

C. two

D. three

Answer: A

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34. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is

A. second

B. more than zero but less than first

C. zero

D. first

Answer: D

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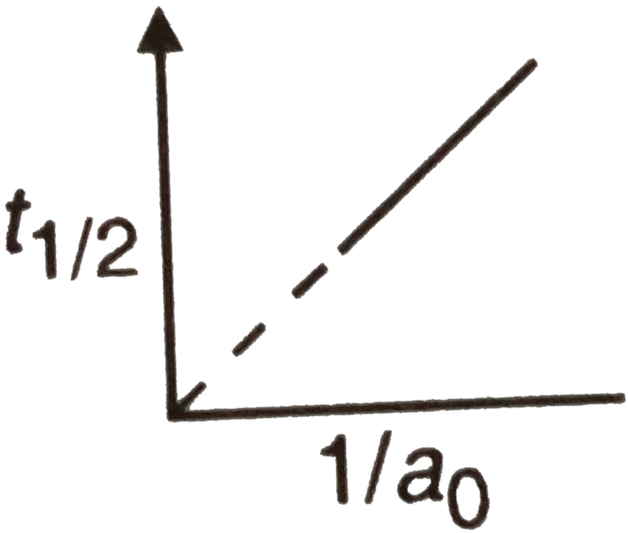
35. The following graph shows how $t_{1/2}$ (half-life) of a reactant R changes with the initial reactant concentration a_0.

The order of reaction will be



A. 0

B. 1

C. 2

D. 3

Answer: C

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36. A reaction $P \rightarrow Q$ is completed 25 % in 25 min, 50 % completed in 25 min if [P] is halved, 25 % completed in 50 min if [P] is doubled. The order of reaction is

A. 1

B. 2

C. 0

D. 3

Answer: C

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37. $t_{1/4}$ can be taken as the time taken for concentration of reactant to drop to $.^{3}/_{4}$ of its initial value. If the rate constant for a first order reaction is K, then $t_{1/4}$ can be written as:

A. $0.10/K$

B. $0.29/K$

C. $0.69 / K$

D. $0.75 / K$

Answer: B

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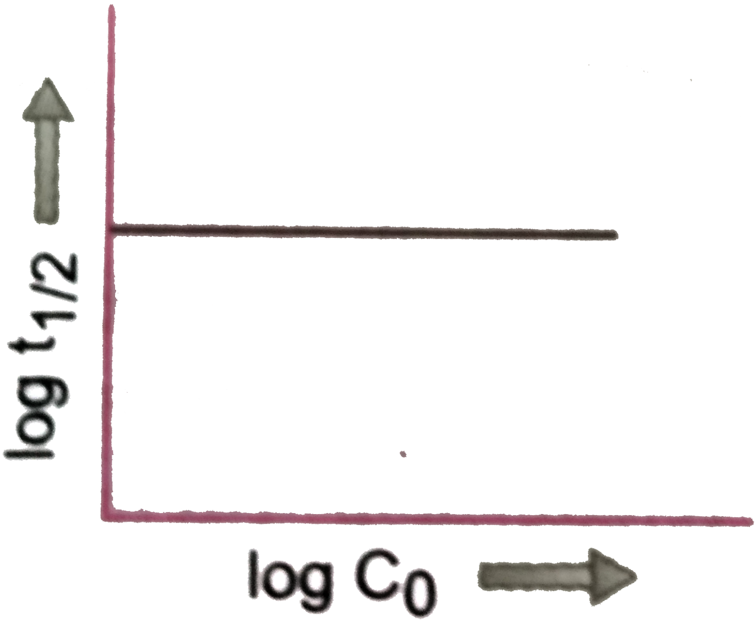
38. A plot of log $t_{1/2}$ versus log C_0 is given in the adjoining fig. The conclusion that can be drawn from this graph is



A. Order $= 1, t_{1/2} = \frac{1}{ka}$

B. Order $= 1, t_{1/2} = \frac{2.303}{k} \log^2$

C. Order $= 0, t_{1/2} = \frac{1}{2 \text{ ka}}$

D. Order $= 2, t_{1/2} = \frac{1}{a}$

Answer: B

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39. For a reation: $A \rightarrow$ Product,

rate law is $-\frac{d[A]}{dt} = K[A]_0$.

The concentration of A left after time t when $t = \frac{1}{K}$ is:

A. $\frac{[A]_0}{e}$

B. $[A]_0 \times e$

C. $\frac{[A]_0}{e^2}$

D. $\frac{1}{[A]_0}$

Answer: A

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40. Decompsition of H_2O_2 follows a frist order reactions. In 50 min the concentrations of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition . When the concentration of H_2O_2 reaches 0.05 M, the rate of fromation of O_2 will be

A. $6.93 \times 10^{-2} \text{ mol min}^{-1}$

B. $6.93 \times 10^{-4} \text{mol L}^{-1} \text{min}^{-1}$

C. $2.66 \text{ L min}^{-1} \text{ at STP}$

D. $1.34 \times 10^{-2} \text{ mol min}^{-1}$

Answer: B

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41. For a first order reaction, the time required for 99.9% of the reaction to take place is nearly

A. 10 times that required for half of the reaction

B. 100 times that required for two-thirds of the reaction

C. 10 times that required for one-fourth of the reaction

D. 20 times that required for half of the reaction

Answer: A

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42. The half-life of a reaction is halved as the initial concentration of the reaction is doubled. The order of the reaction is

A. 0.5

B. 1

C. 2

D. 0

Answer: C

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43. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $k_1 = 1.26 \times 10^{-4} s^{-1}, k_2 = 3.8 \times 10^{-5} s^{-1}$ The percentage distribution of B and C are

A. 75% B and 25% C

B. 80% B and 20% C

C. 60% B and 40% C

D. 76.83% B and 23.17% C

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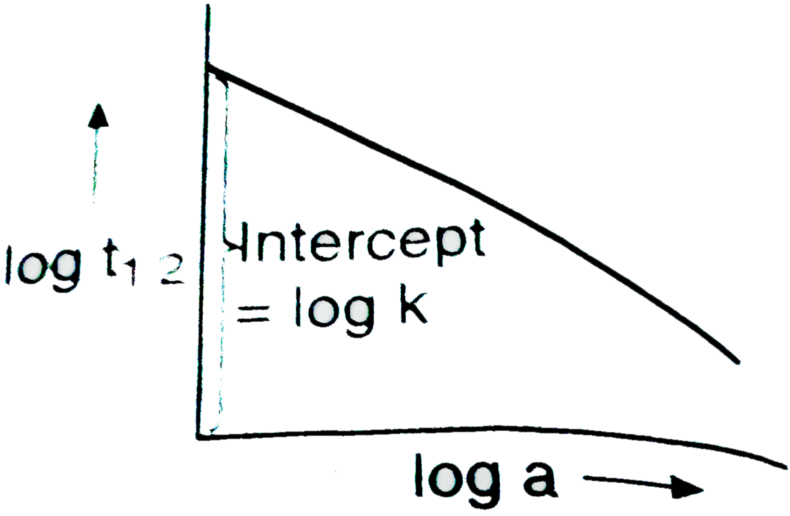
44. For a second order reaction, $2A \rightarrow$ Products, a plot of log $t_{1/2}$ vs log a (where a is initial concentration) will give an intercept equal to which one of the following?



A. $1/k$

B. $\log(1/2\quad k)$

C. $\log(1/k)$

D. $\log k$

Answer: D

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45. Under the same reaction conditions, the intial concentration of $1.386 mol dm^{-3}$ of a substance becomes half in $40s$ and $20s$ theough first order and zero order kinetics, respectively.

The ratio (k_1/k_0) of the rate constants for first order (k_1) and zero order (k_0) of the reaction is

A. $0.5\ \text{mol}^{-1}\ \text{dm}^3$

B. $1.0\ \text{mol dm}^{-3}$

C. $1.5\ \text{mol dm}^{-3}$

D. $2.0\ \text{mol}^{-1}\ \text{dm}^3$

Answer: A

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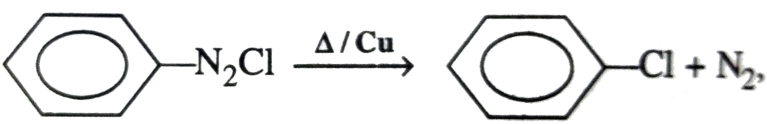
46. In the catalysed decomposition of benzene diazonium chloride,



half-life period is found to be independent of the initial concentration of the reactant. After 10 minutes, the volume of N_2 gas collected is 10 L and after the reaction is complete, it is 50 L. Hence, rate constant of the reaction (in $\min^{-1}$) is

A. $\frac{2.303}{10} \log \frac{10}{50}$

B. $\frac{2.303}{10} \log \frac{50}{50 - 10}$

C. $\frac{2.303}{10} \log \frac{50}{10}$

D. $\frac{2.303}{10} \log \frac{10}{50 - 10}$

Answer: B

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47. Kinetics of the reaction $A(g) \rightarrow 2 \ \mathrm{B}(g) + C(g)$ is followed by measuring the total pressure at different times. It is given that

Initial pressure of A = 0.5 atm.

Total pressure of A after 2 hours = 0.7 atm.

Rate constant of the reaction $= 1 \times 10^{-3} s^{-1}$

What is the rate of reaction $-\frac{d[A]}{dt}$ when the total pressure is 0.7 atm ?

A. $2.0 \times 10^{-4} \ \mathrm{M\,s^{-1}}$

B. $4.0 \times 10^{-4} \ \mathrm{M\,s^{-1}}$

C. $5.0 \times 10^{-4} \ \mathrm{M\,s^{-1}}$

D. $7.0 \times 10^{-4} \ \mathrm{M\,s^{-1}}$

Answer: B

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48. For the non-stoichiometric reaction :

$2\ \mathrm{A} + \mathrm{B} \ \rightarrow \ \mathrm{C} + \mathrm{D}$, the following kinetic data were obtained in three separate experiments all at 298 K

The rate law for the formation of C is

A. $\frac{dC}{dt} = k[A]$

B. $\frac{dC}{dt} = k[A][B]$

C. $\frac{dC}{dt} = k[A]^2[B]$

D. $\frac{dC}{dt} = k[A][B]^2$

Answer: A

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49. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction will respect to M is

A. 4

B. 3

C. 2

D. 1

Answer: B

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50. The rate of a first-order reaction is $0.04\text{mol L}^{-1}s^{-1}$ at 10 seconds and $0.03\text{mol L}^{-1}s^{-1}$ at 20 seconds after initiation of the reaction. The hlaf-life period of the reaction is :

A. $44.1 \quad \text{s}$

B. $54.1 \quad \text{s}$

C. $24.1 \quad \text{s}$

D. $34.1 \quad \text{s}$

Answer: C

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51. For the first-order reaction T_{av} (average life), T_{50} and T_{75} in the increasing order are :

A. $t_{50} < t_{av} < t_{75}$,

B. $t_{50} < t_{75} < t_{av}$,

C. $t_{av} < t_{50} < t_{75}$,

D. $t_{av} = t_{50} < t_{75}$,

Answer: A

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52. In the study of inversion of sucrose in presence of acid, if r_0, r_1 and r_∞ represent the polarimetric readings at times 0, t and ∞ respectively, then at the 50% inversion, which of the following relationship will hold good ?

A. $r_t = r_0 + r_\infty$

B. $r_t = \frac{1}{2}(r_0 + r_\infty)$

C. $r_t = r_0 - r_\infty$

D. $r_t = \frac{1}{2}(r_0 - r_\infty)$

Answer: B

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53. Number of natural life times (T_{av}) required for a first order reaction to achieve 99.9% level of comletion is

A. 6.93

B. 2.31

C. 9.2

D. infinite

Answer: A

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54. Half-life period of a first order reaction is 100 min. After 144.3 min, concentration of reactant is reduced to ... of the original concentration

A. $40\ \%$

B. $30\ \%$

C. $1/e$

D. $1/e^2$

Answer: C

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55. The activation energy of a reaction can be determined from the slop of which of the following graph ?

A. ln k vs $\frac{1}{T}$

B. $\frac{T}{\ln \mathrm{k}} \mathrm{vs} \frac{1}{T}$

C. ln k vs T

D. $\frac{\ln \mathrm{k}}{T} \mathrm{vs} T$

Answer: A

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56. The rate of a reaction doubles when its temperature changes form $300K$ to $310K$. Activation energy of such a reaction will be:

$\left(R = 8.314JK^{-1}mol^{-1} \text{ and } \log 2 = 0.301\right)$

A. 60.5 kJ mol^{-1}

B. 53.6 kJ mol^{-1}

C. 48.6 kJ mol^{-1}

D. 58.5 kJ mol^{-1}

Answer: B

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57. The rate constant of a first orrder reaction becomes six times when the temperature is raised from 350 K to 400 K. Calculate the activation energy of the reaction $\left(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}\right)$

A. 4.17 kJ mol^{-1}

B. 41.7 kJ mol^{-1}

C. $417.0 \text{ kJ mol}^{-1}$

D. $417.0 \text{ kJ mol}^{-1}$

Answer: B

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58. A reactant (A) forms two products

$A \xrightarrow{k_1} B$, Activation energy E_{a1}

$A \xrightarrow{k_2} C$, Activation energy E_{a2}

If $E_{a_2} = 2E_{a_1}$ then k_1 and k_2 are related as

A. $k_1 = 2k_2 e^{Ea_2/RT}$

B. $k_2 = k_1 e^{Ea_1/RT}$

C. $k_2 = k_1 e^{Ea_2/RT}$

D. $k_1 = A \ \ \mathrm{k}_2 e^{Ea_1/RT}$

Answer: D

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59. In the presence of catalyst, the activation energy of the reaction is lowered by 2 kcal at $27^\circ C$. The rate of reaction will increased by

A. 2 times

B. 14 times

C. 28 times

D. 20 times

Answer: C

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60. The rate constant of a reaction at temperature 200 K is 10 times less than the rate constant at 400 K. What is the activation energy (E_a) of the reaction ? (R = gas constant)

A. $1842.4 \quad \mathrm{R}$

B. $921.2 \quad \mathrm{R}$

C. $460.6 \quad \mathrm{R}$

D. $230.3 \quad \mathrm{R}$

Answer: B

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61. The formation of H_2O_2 in the upper atmosphere follows the mechanism

$H_2O + O \rightarrow 2OH \rightarrow H_2O_2$

$\Delta H = 72 \quad \mathrm{kJ} \quad \mathrm{mol}^{-1}, E_a = 77 \quad \mathrm{kJ\ mol}^{-1}$

E_a for the backward process is

A. $5 \quad \mathrm{kJ\ mol}^{-1}$

B. $-5 \quad \mathrm{kJ\ mol}^{-1}$

C. $149 \quad \text{kJ mol}^{-1}$

D. $-149 \quad \text{kJ mol}^{-1}$

Answer: A

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62. For an endothermic reaction, where ΔH represents the enthalpy of reaction in $kJmol^{-1}$, the minimum value for the energy of activation will be

A. less than ΔH

B. zero

C. more than ΔH

D. $equal \rightarrow$ DeltaH`.

Answer: C

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63. When a catalyst increases the rate of a chemical reaction, the rate constant

A. remains constant

B. increases

C. decreases

D. may increase or decrease depending on the order of reaction

Answer: B

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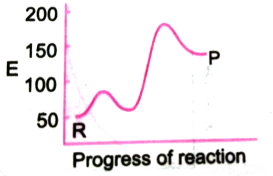
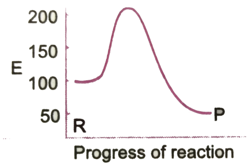
64. An exothermic chemical reaction proceeds by two stages reactants $\xrightarrow{\text{Stage I}}$ intermdediate $\xrightarrow{\text{Stage II}}$ products, The activation energy of stage I is $50 kJmol^{-1}$. The overall enthalpy change of the reaction is -100kJ mol^{-1}. Which diagram could represent the energy level diagram for the reaction ?

A.

B. 

C.

D. 

Answer: C

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65. For a reaction taking place in three steps, the rate consatnt are k_1, k_2 and k_3. The oveall constant $k = \frac{k_1 k_2}{k_3}$. If the energy of activation values of for the first, second and third stage are 40,50 and 60 kJ mol^{-1} is :

A. 30

B. 150

C. 50

D. 60

Answer: A

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66. The rate constant k_1 and k_2 for two different reactions are $10^{16}e^{-2000/T}$ and $10^{15}e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is

A. $1000K$

B. $\frac{2000}{2.303}K$

C. $2000K$

D. $\frac{1000}{2.303}K$

Answer: D

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67. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (K) was found to follow the equation log $k = -(2000)\frac{1}{T} + 6.0$. The pre- exponential factor A and the activation energy E_a, respectively, are :

A. $1.0 \times 10^6 s^{-1}$ and 9.2 kJ mol^{-1}

B. 6.0 s^{-1} and 16.6 kJ mol^{-1}

C. $1.0 \times 10^{-1} s^{-1}$ and 16.6 kJ mol^{-1}

D. $1.0 \times 10^6 s^{-1}$ and 38.3 kJ mol^{-1}

Answer: D

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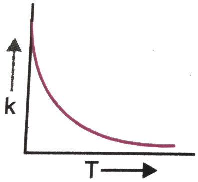
68. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows the Arrhenius equation is

A.

B.

C. 

(c)

D.

Answer: A

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69. The activation energy for a reaction at temperature T K was found to be $2.303 \ \ \mathrm{RT\,J\,mol}^{-1}$. The ratio of the rate constant to Arrhenius factor is

A. 10^{-1}

B. 10^{-2}

C. 2×10^{-3}

D. 2×10^{-2}

Answer: A

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70. Two reactions R_2 and R_2 have identical pre - exponential factors. Activations enery of R_1 exceeds that of R_2 by 10 kJ mol_{-1} . If k_1 and k_2 are rate constants for rate constants for reactions R_1 and R_2 respectively at 300k , then In $\left(\frac{k_2}{k_1}\right)$ is equal to $(R = 8.314 J mol^{-1} K^{-1})$

A. 6

B. 4

C. 8

D. 12

Answer: B

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71. Which one of the following is not correct ?

A. Every bimolecular collision does not result into a chemical reaction

B. Collision theory is not applicable unimolecular reaction

C. According to collision frequency, $k = PZ_{AB}e^{-E/RT}$ where Z_{AB} is collision frequency and P is steric factor

D. Collision theory assumes molecules to be hard spheres

Answer: B

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72. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600K when 20% by mass of N_2O_4(g) decomposes to NO_2(g). The resultant pressure is:

A. 1.2 atm

B. 2.4 atm

C. 2.0 atm

D. 1.0 atm

Answer: B

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73. Consider the following statements.

i) Increase in concentration of rectant increases the rate of a zero order reaction.

ii) rate constant k is equal to collision frequency a if $E_a = 0$

iii) rate constant k is equal to collision frequency A if $E_a = \infty$.

iv) In k vs T is a straight line.

v) In k vs $1/T$ is a straight line.

Correct statements are:

A. (i) and (iv)

B. (ii) and (v)

C. (iii) and (iv)

D. (ii) and (iii)

Answer: B

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74. The oxidation of certain metal is found to obey the equation $A^2 = \alpha t + \beta$, where A is the thickness of the oxide film at time t, α and β are constants. What is the order of this reaction?

A. 0

B. 1

C. -1

D. 2

Answer: C

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75. The decomposition of phosphine $[PH_3]$ on tungsten at low pressure is a first-order reaction. It is because the

A. rate is independent of surface coverage

B. rate of decomposition is very low

C. rate is proportional to the surface coverage

D. rate is inversely proportional to the surface coverage

Answer: C

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (II. Multiple Choice Questions)

1. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid $(HA, 1M)$ is $1/100th$ of that of a strong acid $(HX, 1M)$, at $25^\circ C$. The $K_a(HA)$ is

A. 1×10^{-4}

B. 1×10^{-5}

C. 1×10^{-6}

D. 1×10^{-3}

Answer: A

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (I. Multiple Choice Questions) With one or more than one correct answers

1. In acidic medium, the rate of reaction between $[BrO_3^-]$ and Br^- ions is given by the expression $-\frac{d[BrO_3^-]}{dt} = k[BrO_3^-][Br^-][H^+]^2$ It means

A. Rate constant of the reaction depends upon the concentration of H^+ ions.

B. Rate of reaction is independent of the concentration of the acid added.

C. The change in pH of the solution will affect the rate of reaction.

D. Doubling the concentration of H^{+} ions will increase the reaction rate by 4 times.

Answer: C::D

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2. The rate constant of a reaction is given by $k = 2.1 \times 10^{10} \exp(-2700 / RT)$. It means that

A. log k vs. $1/T$ will be a straight line with slope

$$= -\frac{2700}{2.303 \text{ R}}$$

B. log k vs. $1/T$ will be a straight line with intercept on log k axis

$$= 2.1 \times 10^{10}$$

C. The number of effective collisions are $2.1 \times 10^{10} \text{ cm}^{-3} \text{ sec}^{-1}$

D. Half life of the reaction increases with increase of temperature.

Answer: A::B

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3. In a hypothetical reaction $X \rightarrow Y$, the activation energy for the forward and the backward reaction are 15 and 9 kJ mol^{-1} respectively. The potential energy of X is 10 kJ mol^{-1}. Then

A. Threshold energy of the reaction is 25 kJ

B. The potential energy of Y is 16 kJ

C. Heat of reaction is 6 kJ

D. The reaction is endothermic.

Answer: A::B::C::D

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4. A catalyst

A. increases the average kinetic energy of the reacting molecules

B. decreases the activation energy

C. alters the reaction mechanism

D. increases the frequency of collisions of the reacting species

Answer: B::C

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5. For the first order reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

A. the concentration of the reactant decreases exponentially with time

B. the half-life of the reaction decreases with increasing temperature

C. the half-life of the reaction depends on the initial concentration of the reactant

D. the reaction proceeds to 99.6% completion in eight half-life duration

Answer: A::B::D

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6. The increase in rate constant of a chemical reaction with increasing temperature is (are) due to the fact (s) that

A. the number of collisions among the reactant molecules increases with increasing temperature

B. the activation energy of the reaction decreases with increasing temperature

C. the concentration of the reactant molecules increases with increasing temperature

D. the number of reactant molecules acquiring the activation energy increases with increasing temperature

Answer: A::D

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7. According to the Arrhenius equation,

A. a high activation energy usually implies a fast reaction

B. rate constant increases with increase in temperature. This is due to greater number of collisions whose energy exceeds the activation energy

C. higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant

D. the pre-exponential factor is a measure of the rate at which collisions occure, irrespective of their energy

Answer: B::C::D

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (I. Multiple Choice Questions) (III. Multiple Choice Questions) Based on Comprehension

1. Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as $k = Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction.

The pre-exponential factor in the Arrhenus equation of second order reaction has the units

A. $\text{mol L}^{-1}s^{-1}$

B. $\text{L mol}^{-1}s^{-1}$

C. s^{-1}

D. dimensionless

Answer: B

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2. Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as $k = Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction. Which of the following plot will be linear ?

A. ln k versus T with - ve slope

B. k versus $1/T$ with - ve slope

C. ln k versus $1/T$ with - ve slop

D. ln k versus $1/T$ with + ve slope.

Answer: C

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3. Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as $k = Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction.

If the rate of reaction grows 15.6 times on increasing the temperature by 30 K, the temperature coefficient of the reaction will be nearly

A. 2

B. 2.5

C. 3.0

D. 3.5

Answer: A

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4. Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as $k = Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction.

If the rate of reaction doubles for 10° rise of temperature from 290 K to 300 K, the activation energy of the reaction will be approximately

A. 40 kJ mol^{-1}

B. 50 kJ mol^{-1}

C. 60 kJ mol^{-1}

D. 70 kJ mol^{-1}

Answer: B

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5. Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as $k = Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction.

If x is the fraction of molecules having energy greater than E_a, it will be given by

A. $x = -\dfrac{E_a}{RT}$

B. ln $x = -\dfrac{E_a}{RT}$

C. $x = e^{E_a/RT}$

D. Any of these.

Answer: B

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6. The progress of the reaction $A \Leftrightarrow nB$ with time is represented in the Fig. below :

The value of n is

A. 1

B. 2

C. 3

D. 1.5

Answer: B

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7. The progress of the reaction $A \Leftrightarrow nB$ with time is represented in the Fig. below :

The equilibrim constant K will be

A. 2

B. 1.2

C. 0.5

D. 6.67

Answer: B

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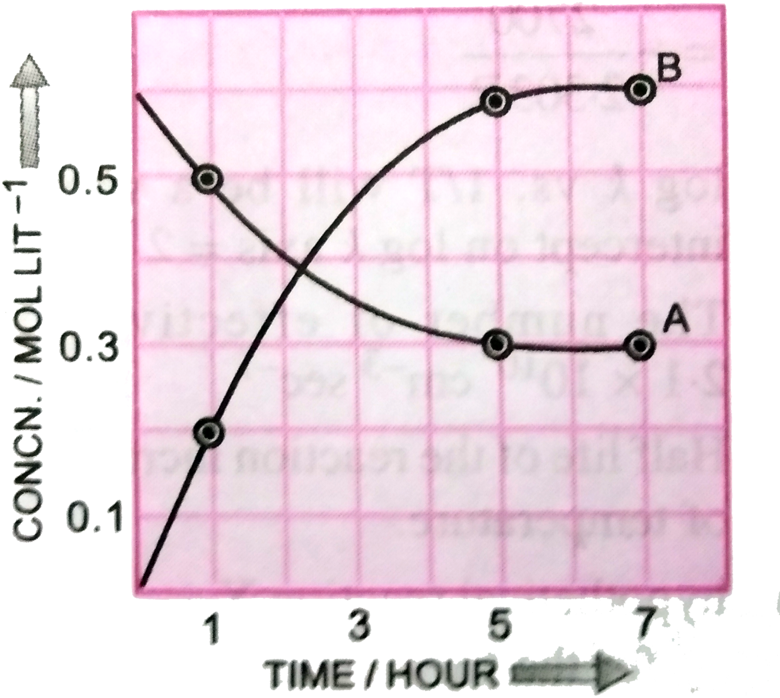
8. The progress of the reaction $A \Leftrightarrow nB$ with time is represented in the Fig. below :



The initial rate of conversion of A will be

A. $0.1 \quad \text{mol L}^{-1} \quad \text{hr}^{-1}$

B. $0.2 \quad \text{mol L}^{-1} \quad \text{hr}^{-1}$

C. $0.4 \quad \text{mol L}^{-1} \quad \text{hr}^{-1}$

D. $0.8 \quad \text{mol L}^{-1} \quad \text{hr}^{-1}$

Answer: A

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1. Match the entries of column I with appropriate entries of column II and choose the correct option out of the four options (a), (b), (c), (d) given at the end of each question.

	Column I (Reaction)		Column II (Order)
(A)	$2\ \mathrm{HI} \rightarrow H_2 + I_2$	(p)	0
(B)	$2\ \mathrm{NH_3} \rightarrow N_2 + 3\ \mathrm{H_2}$	(q)	1
(C)	$2\ \mathrm{H_2O_2} \rightarrow 2\ \mathrm{H_2}O + O_2$	(r)	$1\frac{1}{2}$
(D)	$COCl_2 \rightarrow CO + Cl_2$	(s)	2

A. $A - q, B - p, C - r, D - s$

B. $A - r, B - p, C - s, D - q$

C. $A - s, B - q, C - r, D - p$

D. $A - s, B - p, C - q, D - r$

Answer: D

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1. Match the entries of column I with appropriate entries of column II and choose the correct option out of the four options (a), (b), (c), (d) given at the end of each question.

	Column I		Column II
(A)	Zero order reactions	(p)	$t_{1/2} \propto \frac{1}{[A]_0}$
(B)	First order reactions	(q)	$t_{100\%} = [A]_0/k$
(C)	second order reactions	(r)	Involves at least two r
(D)	Pseudounimolecular reactions	(s)	$[A] = [A]_0 e^{-kt}$

A. $A - s, B - q, C - p, D - r$

B. $A - p, B - r, C - q, D - s$

C. $A - q, B - s, C - p, D - r$

D. $A - r, B - p, C - s, D - q$

Answer: C

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2. Match the entries of column I with appropriate entries of column II and choose the correct option out of the four options (a), (b), (c), (d) given at the end of each question.

	Column I		Column
(A)	Linear plot passing through the origin	(p)	Conc. [
(B)	Linear horizontal plot	(q)	$1/[A]$
(C)	Linear plot with -ve slope and an intercept	(r)	$t_{1/2}$ vs
(D)	Linear plot with + ve slope and an intercept	(s)	$t_{1/2}$ vs

A. $A-s, B-r, C-p, D-q$

B. $A-p, B-s, C-r, D-q$

C. $A-q, B-s, C-p, D-r$

D. $A-s, B-p, C-q, D-r$

Answer: A

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (V. Matrix-Match Type Questions)

1. Match the entries of column I with appropriate entries of column II. Each entry in column I may have one or more than one correct option from column II. If the correct matches are A-p, s , B-r , C-p, q , D-s, then the correctly bubbled 4×4 matrix should be as follows :

	Column I (Units/Property)		Column I
(A)	$\text{mol L}^{-1} s^{-1}$	(p)	Zero ord
(B)	$\text{L mol}^{-1} s^{-1}$	(q)	First ord
(C)	Does not depend upon initial concentration	(r)	second o
(D)	Affected by temperature	(s)	Rate of r

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COMPETITION FOCUS (V. Matrix-Match Type Questions)

1. Match the entries of column I with appropriate entries of column II. Each entry in column I may have one or more than one correct option from column II. If the correct matches are A-p, s , B-r , C-p, q , D-s, then the correctly bubbled 4×4 matrix should be as follows :

	Column I		Co
(A)	Rate constant of an exothermic reaction	(p)	inc
(B)	Rate constant of an endothermic reaction	(q)	dec
(C)	Equilibrium constant of an exothermic reaction	(r)	not
(D)	Equilibrium constant of an endothermic reaction	(s)	not

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (VI. Integer Type Questions)

1. The order of the reaction

$5\ \mathrm{Br}^{-}(aq) + BrO_3^{-}(aq) + 6\ \mathrm{H}^{+}(aq) \rightarrow 3\ \mathrm{Br}_2(aq) + 7\ \mathrm{H}_2O(l)$ is

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2. The half-life period of a 3rd order reaction is found to be 1 hour when we start with a concentration of $0.3\ \mathrm{mol\,L}^{-1}$ of the reactant. If we start with $0.1\ \mathrm{mol\,L}^{-1}$, the half-life period in hours will be

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3. In the reaction $\mathrm{a\,A+b\,B} \rightarrow$ Products, if only concentration of A is doubled the rate becomes quadrupled and if further the vessel is reduced to half the volume, the rate becomes 8 times. The overall order of reaction is

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4. Starting with an initial pressure of 5 atm of azoisopropane, 40% of it decomposes into nitrogen and hexane vapours in one hour. The pressure in atm exerted by the mixture in atm at this time will be

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5. How many times the rate of reaction will change if temperature is increased from $20^\circ C$ to $50^\circ C$?

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6. After 24 hour, only 0.125 g out of the initial quantity of 1 g of a radioactive isotope remains behind. The half-life period of the radioactive

isotope in hours is

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7. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained :

The order of the reaction is

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (VI. Integer Type Questions)

1. An organic compound undergoes first decompoistion. The time taken for its decompoistion to $1/8$ and $1/10$ of its initial concentration are $t_{1/8}$ and $t_{1/10}$, respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? $(\log_{10} 2 = 0.3)$

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (VII. Assertion-Reason Type Questions) Type - I

1. Statement-1. The dissociation of NH_3 on hot platinum surface may be reaction of zero order or first order.

Statement-2. Pressure of the gas affects the order of reaction.

A. Statement-1 is True, Statement-2 is True , Statement-1 is a correct explanation of Statement-1.

B. Statement-1 is True, Statement-2 is True , Statement-2 is NOT the correct explanation of Statement-1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True.

Answer: A

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2. Statement-1. In the reaction, $N_2 + 3\ \mathrm{H}_2 \rightarrow 2\ \mathrm{NH}_3$, the rate of reaction is different in terms of N_2, H_2 and NH_3.

Statement-2. Rate of disappearance of N_2 and H_2 and rate of formation of NH_3 are not equal to each other.

A. Statement-1 is True, Statement-2 is True , Statement-1 is a correct explanation of Statement-1.

B. Statement-1 is True, Statement-2 is True , Statement-2 is NOT the correct explanation of Statement-1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True.

Answer: D

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3. Statement-1. Rate constant of a zero order reaction has same units as the rate of reaction.

Statement-2. Rate constant of a zero order reaction does not depend upon the units of concentration.

A. Statement-1 is True, Statement-2 is True , Statement-1 is a correct explanation of Statement-1.

B. Statement-1 is True, Statement-2 is True , Statement-2 is NOT the correct explanation of Statement-1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True.

Answer: C

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4. Statement-1. In a zero order reaction, if concentration of the reactant is doubled, half-life period is also doubled.

Statement-2. The total time taken for a zero order reaction to complete is double of the half-life period.

A. Statement-1 is True, Statement-2 is True , Statement-1 is a correct explanation of Statement-1.

B. Statement-1 is True, Statement-2 is True , Statement-2 is NOT the correct explanation of Statement-1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True.

Answer: B

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5. Assertion (A) : The rate constant of a pseudo unimolecular reaction has the units of a first order reaction. Reason (R): A pseudo unimolecular reaction is a reaction of first order in which one of the reactant is present in large excess.

A. Statement-1 is True, Statement-2 is True , Statement-1 is a correct explanation of Statement-1.

B. Statement-1 is True, Statement-2 is True , Statement-2 is NOT the correct explanation of Statement-1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True.

Answer: A

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6. Assertion: 50% of reaction is completed in $50\,\text{sec}$, therefore, 75% of the reaction will be completed in $75\,\text{sec}$.

Reason: The rate constant of a zero order reaction depends uopn time as $k = \frac{1}{t}\{[A]_0 - [A]\}$.

A. Statement-1 is True, Statement-2 is True , Statement-1 is a correct explanation of Statement-1.

B. Statement-1 is True, Statement-2 is True , Statement-2 is NOT the correct explanation of Statement-1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True.

Answer: C

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (VII. Assertion-Reason Type Questions) Type - II

1. Assertion. In any reaction, the rate of disappearance of a reactant is same as the rate of reaction.

Reason. Both rate of reaction and rate of disappearance of a reactant represent decrease in the concentration of a reactant per unit time.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: D

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2. Assertion. Rate constant of a zero order reaction has the same units as those of the rate of reaction.

Reason. For a zero order reaction, Rate = Rate constant.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: A

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3. Assertion. Order of a reaction can be fractional but molecularity is never fractional.

Reason. Order of reaction does not depend upon the stoichiometric coefficients of the balanced equation.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: A

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4. Assertion. The molecularity of the reaction $H_2 + Br_2 \rightarrow 2 \text{ HBr is } 2.$

Reason. The order of the reaction is $3/2$.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: B

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5. Assertion. The order of a reaction can have fractional value.

Reason. The order of reaction cannot be written from the balanced equation of the reactant.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: B

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6. Assertion. Half-life of a reaction is independent of the initial concentration of the reactant.

Reason. Half-life of a reaction is independent of the order of reaction.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: D

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7. Assertion (A) : For a first order, the concentration of a reaction decreases exponentially with time.

Reason (R): The rate of reaction at any time depends upon the concentration of the reactant at that time.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: B

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8. Assertion (A): For the reaction

$RCl + NaOH(g) \rightarrow ROH + NaCl$, the rate of reaction is reduced to half on reducing the cocentration of RCl to half.

Reason (R): The rate of the reaction is represented by $k[RCl]$, i.e., it is a first order reaction.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: C

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9. Assertion : The hydrolysis of methyl acetate by dil. HCl is a pseudo first order reaction

Reason : HCl acts as a catalyst for the hydrolysis .

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: B

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10. Assertion. Average life of a radioactive element is that period in which 63% of it is decayed.

Reason. Average life $\tau = 1.44 \ \mathrm{t}_{1/2}$.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: A

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11. Assertion. By 10° rise of temperature, the rate of reaction increases by 100% to 200%.

Reason. By 10° rise of temperature, the collision frequency increases by 100 to $200\,\%$.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: C

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12. Assertion: A catalyst increases the rate of a reaction.

Reason: In presence of a catalyst, the activation energy of the reaction decreases.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: D

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13. Assertion. According to collision theory, rate of reaction does not depend on the total number of collisions.

Reason. The overall rate of reaction depends upon the number of effective collisions.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: C

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14. According to the tranistion state theory, for the formation of on activation complex, one of the vibrational degree of freedom is converted into the tranistion degree of freedom.

Reason (R): The energy of the activated complex is higher than the energy of the reactant molecules.

A. If both assertion and reason are true and reason is the true explanation of the assertion.

B. If both assertion and reason ae true but reason is not the true explanation of the assertion.

C. If assertion is true, but reason is false.

D. If both assertion and reason are false.

Answer: A

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COMPETITION FOCUS (JEE(Main and Advanced)/Medical Entrance) (VIII. Multiple Choice Questions)

1. In the study of oxidation of iodide ions by hydrogen peroxide in presence of an acid and starch as a clock reaction,

A. thiosulphate added should be in large amount

B. thiosulphate added should be in small amount

C. amount of thiosulphate added has no importance

D. thiosulphate is added to speed up the reaction

Answer: B

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2. In the study of oxidation of iodide ions by hydrogen peroxide in presence of dilute H_2SO_4 and starch as a clock reaction, if excess of thiosulphate is added

A. blue colour will appea immediately

B. blue colour will not appear at all

C. blue colour will appear only on heating the reaction mixture

D. blue colour will appear after a very long time

Answer: B

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3. In the study of oxidation of iodide ions by hydrogen peroxide in presence of dilute H_2SO_4, thiosulphate and starch as a clock reaction, if concentration of iodide ions is increased

A. less time will be taken for blue color to appear

B. more time will be taken for blue colour to appear

C. same time will be taken for blue colour to appear

D. any one of the above can happen depending upon the amount of H_2SO_4 present.

Answer: A

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IMPORTANT QUESTIONS FOR BOARD EXAMINATION

1. For a reaction $A \rightarrow B$, the rate of reaction can be denoted by $-\frac{dA}{dt}$ or $+\frac{dB}{dt}$. State the significance of plus and minus signs in this case.

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2. For the reaction $N_2(g) + 3\ \mathrm{H}_2(g) \rightarrow 2\ \mathrm{NH}_3(g)$, if $\Delta[NH_3]/\Delta t = 4 \times 10^{-8} \mathrm{mol\ L}^{-1} s^{-1}$ what is the value of $-\Delta[H_2]/\Delta t$?

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3. A chemical reaction $2A \rightarrow 4B + C$ in gas phase occurs in a closed vessel. The concentration of B is found to increase by 5×10^{-3} mol L^{-1} in 10 seconds. Calculate i) the rate of appearance of B ii) the rate of disappearance of A.

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4. Identify the reaction order from the following rate constant :

$k = 2.3 \times 10^{-5} \text{ litre mol}^{-1}\text{sec}^{-1}$

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5. When is the of reaction equal to specific reaction rate ?

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6. The conversion of molecules X to Y follows second order kinetics. If the concenration of X is increased to three times, how will it affect the rate of formation of Y ?

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7. The rate constant for an isomerisation reaction, $A \rightarrow B$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the initial concentration of A is 1 M, calculate the rate of reaction after 1 h.

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8. The rate of a gaseous reaction is halved when the volume of the vessel is doubled. What is the order of reaction ?

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9. Write any four differences between 'rate of reaction' and 'rate constant' of a reaction.

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10. (a) For a reaction, the rate law is : Rate $= k = [A][B]^{1/2}$. Can this reaction be an elementary reaction ?

(b) The possible mechanism for the reaction : $2 \ \mathrm{H}_2 + 2 \ \mathrm{NO} \rightarrow N_2 + 2 \ \mathrm{H}_2 O$ is

(i) $2 \ \mathrm{NO} \Leftrightarrow \mathrm{N_2O_2}$ (ii) $N_2O_2 + H_2 \rightarrow N_2O + H_2O \ \ (\text{slow})$ (iii) $N_2O + H_2 \rightarrow N_2 + H_2O \ \ (\text{fast})$

What is (i) the rate law for the reaction (ii) order of the reaction.

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11. Calculate the half life period for zero order reaction..

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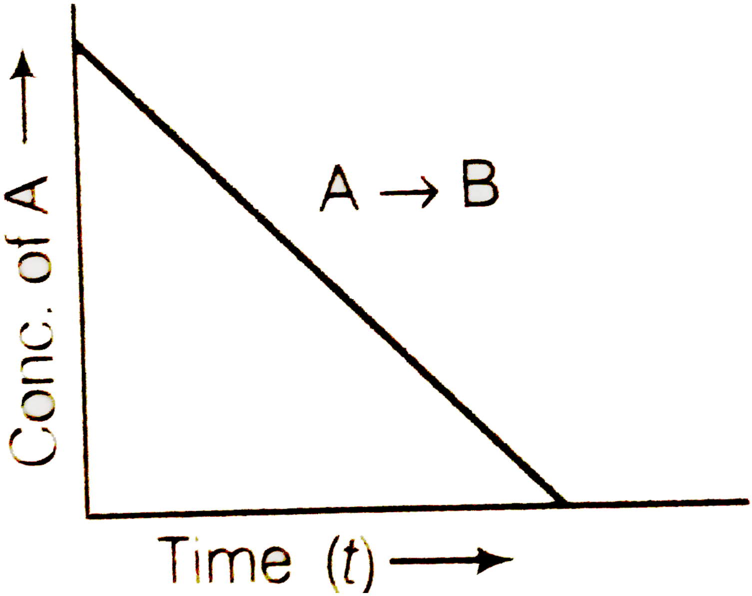
12. For a general reaction $A \rightarrow B$, plot of concentration of A vs time is given in figure. Answer the following questions on the basis of this graph.

(i) what is the order of the reaction?

(ii) What is the slope of the curve ?

(iii) What are the units of rate constant?



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13. (a) Derive the equation for the rate constant of a first order reaction and show that the time required for the completion of half of the first order reaction is independent of initial concnetration.

(b) Show that in case of a first order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction.

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14. The thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minutes, how long it take for 90% of the compounds to decompose.

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15. The rate of a first order reaction is 0.04 mol $\text{litre}^{-1}s^{-1}$ after 10 minutes and 0.03 mol $\text{litre}^{-1}s^{-1}$ after 20 minutes. Find the half life period of the reaction.

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16. For the decomposition of azoisopropane to hexane and nitrogen at 54 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rare constant.

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17. During nuclear explosion, one of the products is $.^{90} Sr$ with half $-$ life of 28.1years. If $1\mu g$ of $.^{90} Sr$ was absorbed in the bones of a newly born baby instead of calcium, how much of its will remain after 10 years and 60 years if it is not lost metabolically.

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18. In the reaction $aA + bB \rightarrow$ products, if concentration of A is doubled (keeping B constant) the initial rate becomes four times and if B is doubled (keeping A constant), the rate becomes double. What is the rate law equation and order of reaction ?

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19. If half-life period of a reaction is inversely proportional to initial concentration of the reactant, what is the order of reaction ?

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20. One-fourth of a first order reaction is completed in 32 minutes. What is the half-life period of this reaction?

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21. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?

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22. (a) What are the units of the rate constant of a pseudo unimolecular reaction ?

(b) Why hydrolysis of ethyl acetate with $NaOH$ is reaction of second order while with HCl, it is of first order ?

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23. (a) Define the term Activation energy. Why different reactions proceed at different speeds ?

(b) Can a reaction have zero activation energy ?

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24. The first order rate constant for the decompoistion of C_2H_5I by the reaction.

$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$

at $600 K is 1.60 \times 10^{-5} s^{-1}$. Its energy of activation is $209 kJ mol^{-1}$. Calculate the rate constant at $700K$

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25. The rate constants of a reaction at 500 K and 700 K are $0.02 s^{-1}$ and $0.07 s^{-1}$ respectively. Calculate the values of E_a and A.

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26. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

$\log k = 14.34 - 1.25 \times 10^4 \mathrm{K} / \mathrm{T}$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes ?

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27. The time required for 10% completion of a first order reaction at $298K$ is equal to that required for its 25% completion at $308K$. If the value of A is $4 \times 10^{10} s^{-1}$, calculate k at $318K$ and E_a.

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28. The reactions $: 2CO(g) = O_2 9g) \rightarrow 2CO_2(g)$ and $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ look to be similar. Yet the former is slower than latter at same temperature. Why ?

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29. (a) Why does the rate of a reaction increase with rise in temperature ?

(b) What is the effect of adding catalyst on the free energy change (ΔG) of a reaction ?

(c) The activation energy of a first order reaction at 300 K is

$60 \ \text{kJ mol}^{-1}$. In the presence of a catalyst, the activation energy is lowered to $50 \ \text{kJ mol}^{-1}$ at the same temperature. How many times the rate of reaction will change ?

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30. What is the Expression for rate constant using collision theory of reaction rates. Compare this result with Arrhenius equation. What are the limitations of collusion theory ?

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ADVANCED PROBLEMS FOR COMPETITIONS

1. A flask contains a mixture of two compounds AB and XY. Both of these decompose on heating by first order reaction. If the half-life of AB is 30 min and that of XY is 10 min, how long will it take for the concentration of

AB to be four times that of XY ? Assume that the initial concentration of both AB and XY to be same.

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2. For a reaction A $\rightarrow$ Products, starting with initial concentrations of 5×10^{-3} M and 25×10^{-4}M, half-lives are found to be 1.0 and 8.0 hour respectively. If we start with an initial concentration of 1.25×10^{-3} M, what will be the half-life of the reaction ?

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3. Two substances A and B are present such that $[A_0] = 4[B_0$ and half-life of A is 5 minutes and that of B is 15 minutes. If they start decaying at the same time following first order kinetics after how much time the concentration of both of them would be same ?

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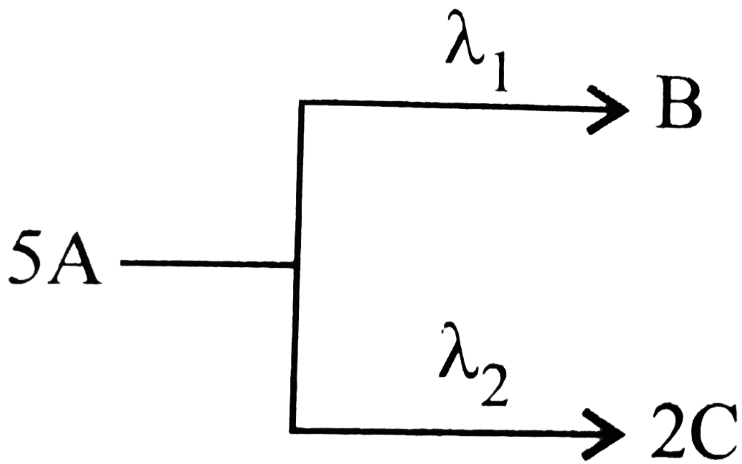
4. A follow parallel path of first-order reactions giving B and C as

If the initial concentration of A is $0.25M$, calculate the concentration of C after 5 hr of reaction.



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5. Given that the enthalpy change of a reaction at 325 K is 0.12 kcal and energy of activation for the backward reaction is 0.02 kcal, calculate the percentage of the reactant molecules, crossing over the energy barrier.

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6. $A(g) \xrightarrow{\Delta} P(g) + Q(g) + R(g)$, follows first order kinetics with a half-life of 69.3 s at $500^{\circ} C$. Starting from the gas A enclosed in a container at $500^{\circ} C$ and at a pressure of 0.4 atm, the total pressure of the system after 230 s will be

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7. A drop of solution (volume $0.05 mL$) contains $3 \times 10^{-6} \text{mole} H^{\oplus}$ ions. If the rate constant of disappearance of $H^{\oplus}$ ions is $1 \times 10^{7} mol L^{-1} s^{-1}$, how long would it take for $H^{\oplus}$ ions in the drop of disappear?

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8. The first order reaction:

Sucrose $\rightarrow$ Glucose + Fructose takes place at $308K$ in $0.5 N HCl$. At time zero the initial total rotation of the mixture is 32.4°. After 10 min, the total rotation is 28.8°. If the rotation of sucrose per mole is 85°, that of glucose is 7.4°, and of fructose is -86.04°, calculate the half life of the reaction.

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9. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant k_1 and k_2 respectively. The energy of activation for the two reactions are $152.30 kJ mol^{-1}$ and $157.7 kg mol^{-1}$ as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

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10. The rate constant for the reaction $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$ is given by

In $\left[k / \overset{-1}{\min}\right] = -11067 / \mathrm{TK} + 31.33$

Calculate the temperature at which the rate of this reaction will be doubled from that at $25^{\circ} C$.

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11. A hydrogenation reaction is carried out at 500 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 energy by 20 kJ mol^{-1} .

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12. The energy change accompanying the equilibrium reaction A $\Leftrightarrow$ B is $-33.0 \text{ kJ mol}^{-1}$. Calculate

(i) Equilibrium constant K_c for the reaction at 300 K

(ii) Energy of activation for forward and backward reaction $\left(E_f \text{ and } E_b\right)$ at 300 K. Given that E_f and E_b are in the ratio 20 : 31.

Assume that pre-exponential factor is same for forward and backward reaction.

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13. Two reaction, $(I) A \rightarrow$ Products and $(II) B \rightarrow$ Products, follow first order kinetics. The rate of reaction (I) is doubled when the temperature is raised form $300K$ to $310K$. The half life for this reaction at $310K$ is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for reaction (II) is twice that of reaction (I), (a) calculate the rate of constant of reaction (II) at $300K$.

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14. A certain reaction $A + B \rightarrow P$ is of first order with respect to each reactant. If $[A]_0 = 0.1 \text{ M}, [B]_0 = 5.0$ M and the second order rate constant k is $6 \times 10^{-3} \text{M}^{-1} s^{-1}$, calculate the half-life period of the reaction in seconds.

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