Chemical Kinetics

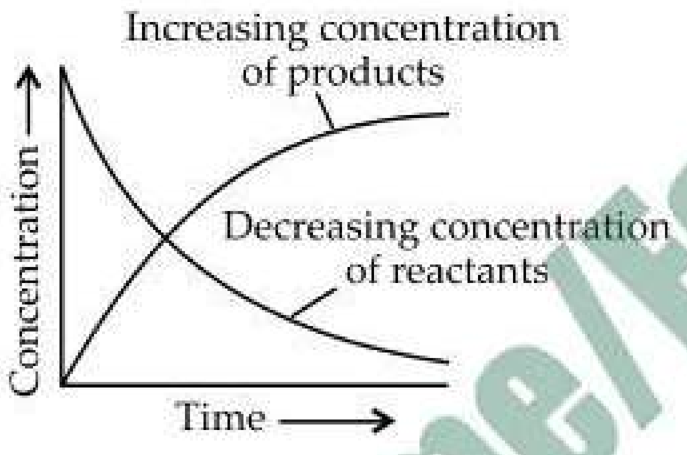
- **Chemical kinetics** is the study of the rate and mechanism of chemical reactions.
- **Rate of reaction** is the change in concentration of reactants or products in unit time.

  For the reaction,

  $2P + 3Q \longrightarrow 4R + 5S$

  $$\text{Rate} = \frac{-1}{2}\frac{d[P]}{dt} = \frac{-1}{3}\frac{d[Q]}{dt} = \frac{1}{4}\frac{d[R]}{dt} = \frac{1}{5}\frac{d[S]}{dt}$$

  - **Unit of rate of reaction :** mol L^{-1} s^{-1}
  - Graph of [reactant] *vs* time; starts at $t = 0$ at high concentration (*i.e.*, $[\text{reactant}]_0$) and [reactant] decreases as time increases.

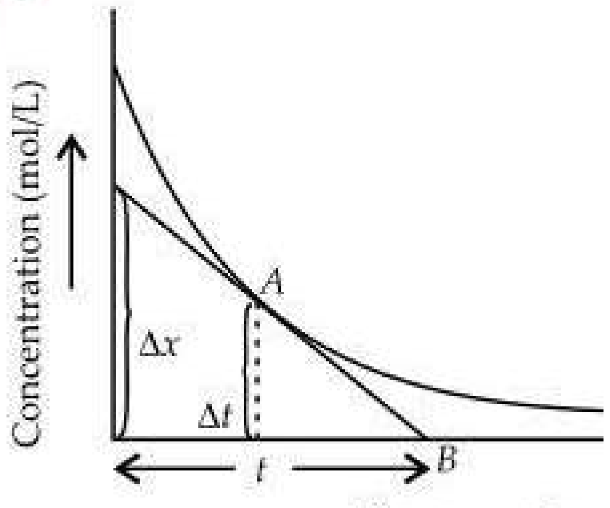
    Graph of [product] *vs* time; starts at $t = 0$ at [product] = 0 and [product] increases as time increases.

    $$A \longrightarrow B$$

    $$\text{Average rate of reaction} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

    $$r_{\text{avg.}} = -\frac{[A_2]-[A_1]}{t_2-t_1} = \frac{[B_2]-[B_1]}{t_2-t_1}$$

  - **Instantaneous rate :** The rate of change of concentration of any one of the reactant or product over a very small interval of time.

    $$r_{\text{inst.}} = \lim_{\Delta t \to 0} -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$$

    $$r_{\text{inst.}} = \frac{\text{Intercept along ordinate}}{\text{Intercept along abscissa}} = \frac{\Delta x}{\Delta t}$$

Factors Affecting Rate of the Reaction

- **Nature of the reactants :**

  Physical state :

  $$\underrightarrow{\text{Gaseous state} > \text{Liquid state} > \text{Solid state}}_{\text{decreasing rate of reaction}}$$

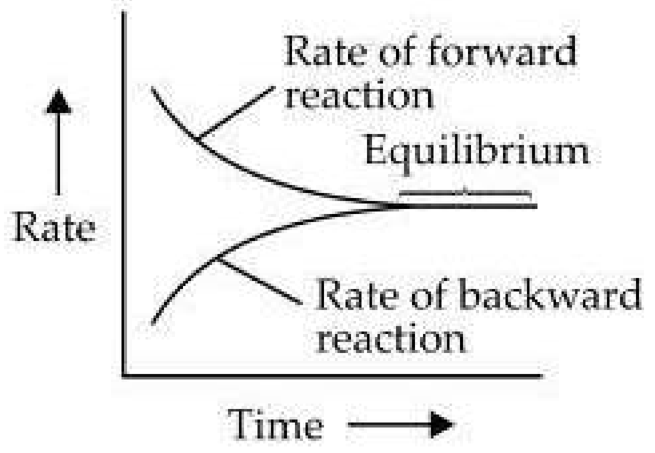
- **Size of reactants :** As size of reactant decreases, rate of reaction increases. Rate of reaction is maximum in powdered state because of increase in surface area.
- **Chemical nature :** Rate of reaction increases if the number of bonds broken and formed in the reactions are lesser in number.
- **Concentration of reactants :**

  $A + B \rightleftharpoons C + D$

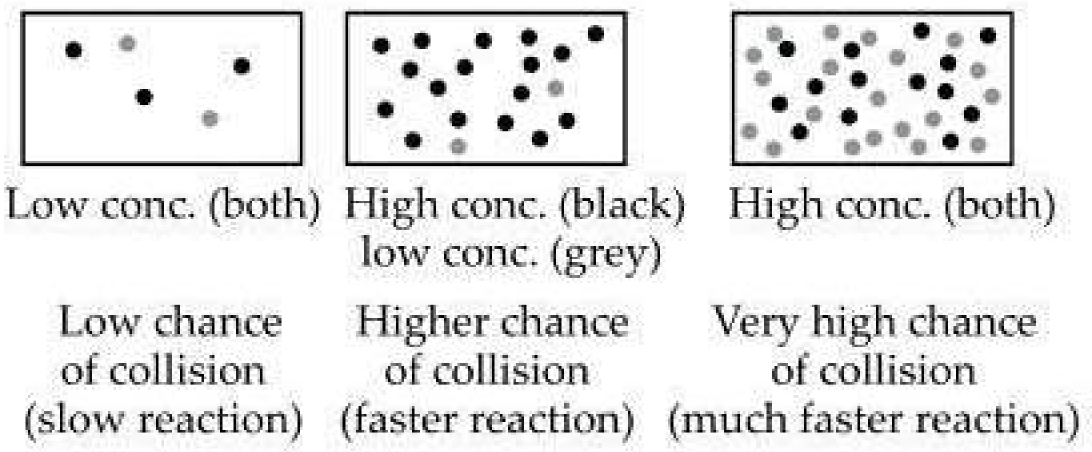
  Rate of forward reaction = $k_f[A][B]$

  Rate of backward reaction = $k_b[C][D]$

  Rate of forward reaction decreases and that of backward reaction increases with passage of time. At equilibrium both the rates become equal.

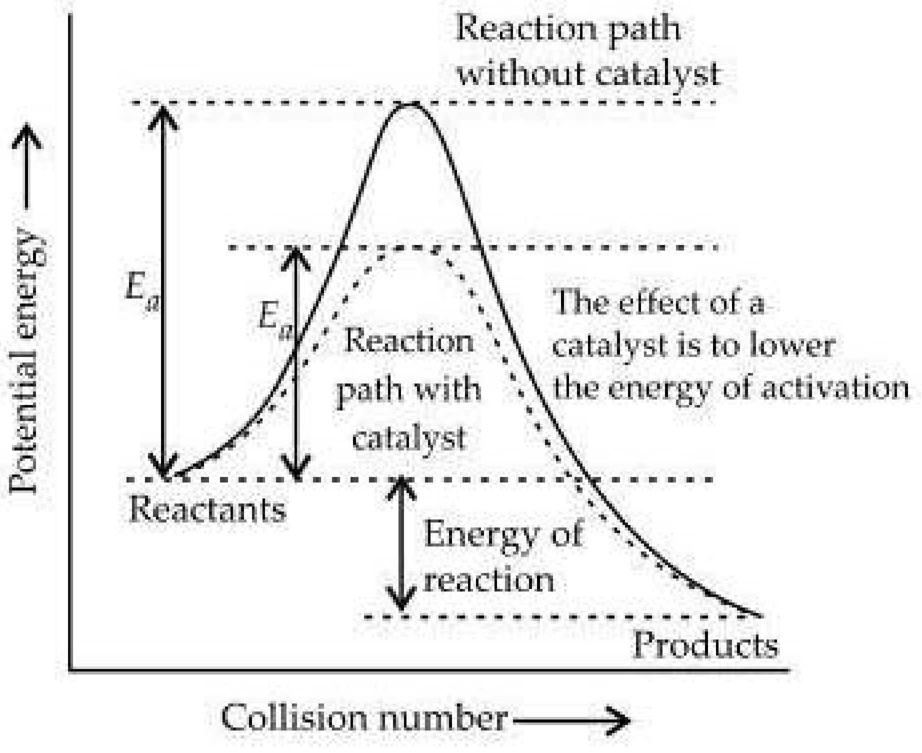
- **Effect of concentration :**

- **Effect of temperature :** The rates of many reactions are approximately doubled or tripled for every 10°C rise in temperature.

  $$\text{Temperature coefficient } (\mu) = \frac{k_{t+10}}{k_t} = 2 \text{ or } 3$$

- **Presence of catalyst :** A positive catalyst increases the reaction rate by changing the path of reaction and lowering the activation energy.

Rate Law and Rate Constant

- **Law of mass action :** The rate of reaction is directly proportional to the product of the active mass (molar concentration) of the reactants raised to powers equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction.

  $A + B \longrightarrow C + D$

  Rate $\propto [A]\,[B]$

  Rate $= k[A]\,[B]$ (law of mass action)

  k = constant of proportionality = rate constant

  $[A] = [B] = 1$, rate of reaction $= k$

  So, rate constant is the rate of the reaction when concentration of each of the reactant is unity. So also known as specific reaction rate.

- **Unit of rate constant :** $\left[\dfrac{1}{\text{mol/litre}}\right]^{n-1} \times \text{time}^{-1}$

  $$= \left(\frac{\text{litre}}{\text{mol}}\right)^{n-1} \text{sec}^{-1}$$

  n = order of reaction.

- **Rate law expression :** Consider a general reaction,

  $aA + bB + cC \longrightarrow$ product

  Rate $= k[A]^a\,[B]^b\,[C]^c$ (law of mass action)

  Rate $= k[A]^p\,[B]^q\,[C]^r$ (rate law expression)

  p, q and r are determined experimentally and may or may not be equal to a, b and c. p, q, r represents the order of reaction with respect to a, b, c.

Order and Molecularity of a Reaction

- **Order of a reaction :** Sum of powers of concentration terms involved in the rate law expression is called order of reaction.

  Consider a reaction :

  $m_1A + m_2B + m_3C \longrightarrow$ product

  Rate $= k[A]^{m_1}\,[B]^{m_2}\,[C]^{m_3}$

  Order of reaction $= m_1 + m_2 + m_3$

- **Molecularity of a reaction :** The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form products is called the molecularity of a reaction.

  $4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$

  $HBr + O_2 \longrightarrow HOOBr$ (R.D. step)

  So molecularity of this reaction is two not five.

	Molecularity	Order
1.	Theoretical concept.	An experimentally determined quantity.
2.	It cannot be zero, fractional, infinite and imaginary.	It can be equal to zero, positive, negative and fractional.
3.	It cannot be greater than three.	Greater than three is also possible.

Integrated Rate Equation

- **Zero order reaction :**

  $$A \longrightarrow \text{products.}$$

  At $t = 0$ $\quad a \quad 0$

  At time t $\quad a - x \quad x$

  Rate law, $\left(\dfrac{dx}{dt}\right) = k_0[A]^0 = k_0$

  $$dx = k_0dt$$

  On integration, $x = k_0t + I$ (Integration constant)

  When $t = 0$, $x = 0$ then $I = 0$.

  $x = k_0t$ or $k_0 = \dfrac{x}{t} = \dfrac{\text{mole/litre}}{\text{sec}}$

  $\therefore$ Unit of k_0 = mol litre^{-1} sec^{-1}

- **First order reaction :**

  $$A \longrightarrow \text{products}$$

  At time $t = 0$ $\quad a \quad 0$

  At time t $\quad (a - x) \quad x$

  Rate $= k_1[A]^1$

  $\dfrac{dx}{dt} = k_1[a - x]^1$

  $\displaystyle\int \frac{dx}{(a-x)} = \int k_1 dt$

  $-\log_e(a - x) = k_1t + I$ (Integer constant)

  If $t = 0$, $x = 0$ then $I = -\log_e(a)$.

  So $-\log_e(a - x) = k_1t - \log_e(a)$

  $k_1t = \log_e \dfrac{a}{(a-x)} \Rightarrow k_1 = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x}$

- **Second order reaction:**

  $$A \quad + \quad A \longrightarrow \quad \text{products}$$

  At $t = 0$ $\quad a \quad a \quad 0$

  At time t $\quad (a - x) \quad (a - x) \quad x$

  Rate $= k_2[A]^2 = k_2(a - x)^2$

  $\dfrac{dx}{(a-x)^2} = k_2dt$

  On integration, $k_2 = \dfrac{1}{t}\dfrac{x}{a(a-x)}$

- **nth order :** $k_n = \dfrac{1}{(n-1)t}\left[\dfrac{1}{(a-x)^{n-1}} - \dfrac{1}{(a)^{n-1}}\right]$

  when $n \geq 2$

- **Half-life period :** Time in which the initial concentration becomes half is known as half-life period.

  $$A \longrightarrow \text{product}$$

  At $t = 0$ $\quad a \quad 0$

  At time $t_{1/2}$ $\quad (a - a/2) \quad a/2$

  Example : zero order reaction, $k_0 = x/t$

  At half-life time, $k_0 = \dfrac{a/2}{t_{1/2}}$ or $t_{1/2} = \dfrac{a}{2k_0}$

  First order reaction, $k = \dfrac{2.303}{t}\log\dfrac{a}{(a-x)}$

  At half-life time,

  $$k = \frac{2.303}{t_{1/2}}\log\frac{a}{0.5a} = \frac{2.303}{t_{1/2}}\log 2$$

  $$k = \frac{0.693}{t_{1/2}} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k}$$

  If n is the order of reaction, then

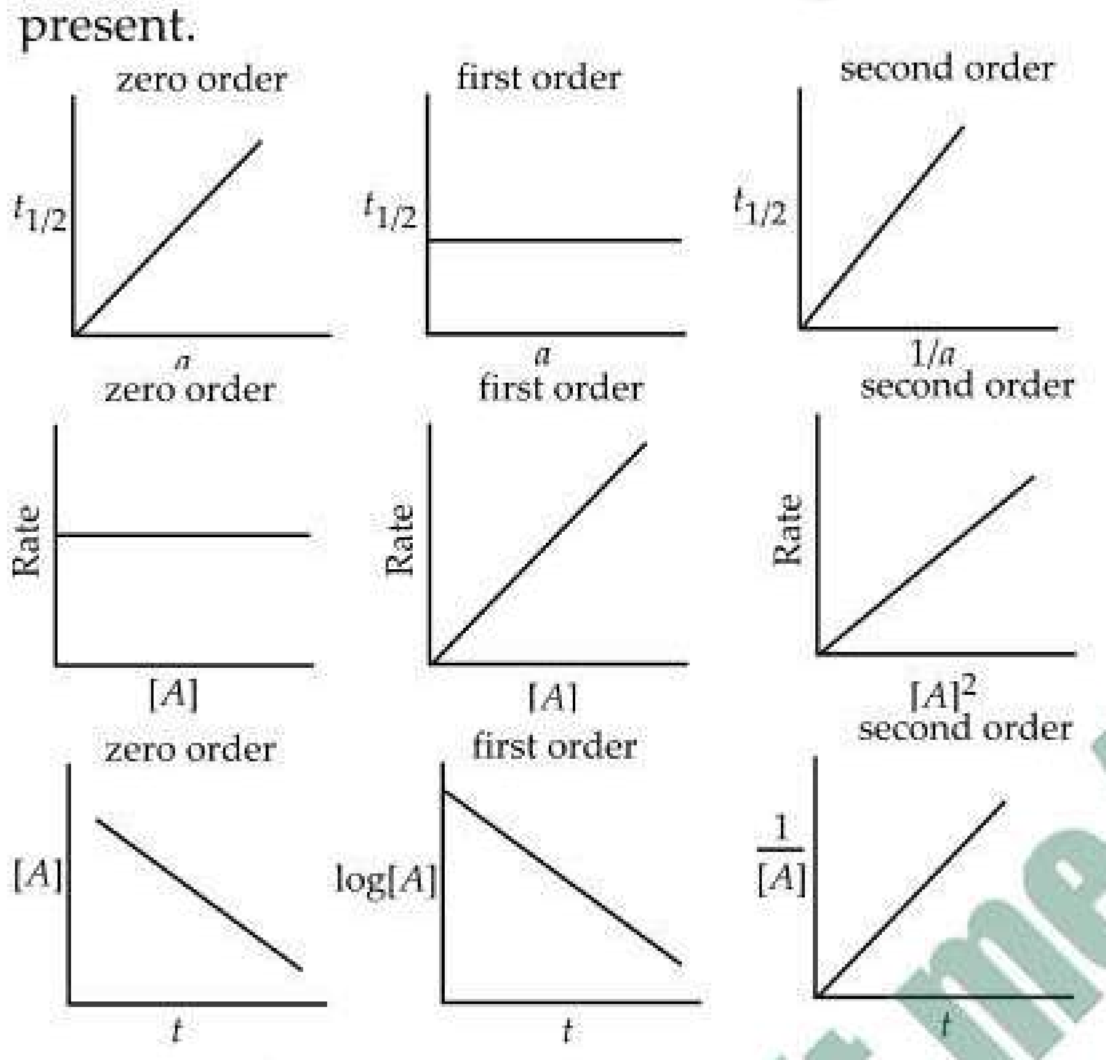
  $$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_n(a)^{n-1}}$$

Rate Law, Integrated Rate Law, Half-life, Unit of Rate constant and Graph for the Reactions of Different order

Order	Rate Law	Integrated Rate Law	Half-life	Unit of Rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L^{-1} s^{-1}	$[A]$ *vs* t; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ *vs* t; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	$t_{1/2} = 1/k[A]_0$	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$	$\frac{1}{[A]^{n-1}}$ *vs* t; slope = k

Experimental Determination of Order of Reaction

- **Graph method :** Used when only one reactant is present.



- **Method of integration :** Calculate the value of k at different time interval with kinetic equations of various order. The equation which gives the most constant value for rate constant (k), is the one corresponding to the order of reaction.
- **Half-life method :** General expression for half-life,

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

n = order of reaction.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

a_1 and a_2 ⇒ two different initial concentrations.
Taking log and rearrangement gives

$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1}$$

- **Arrhenius equation :**

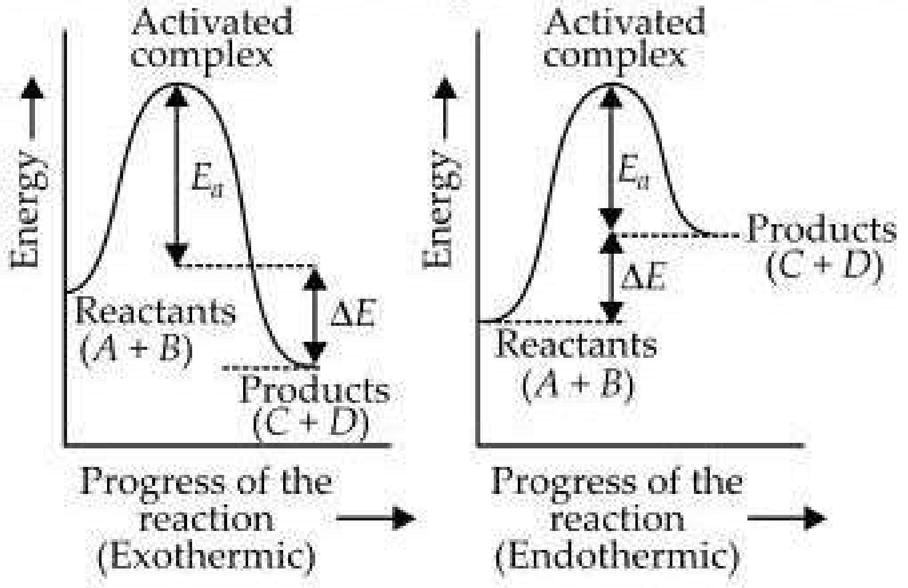
$$k = Ae^{-E_a/RT}$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\,RT}$$

where k = rate constant, A = pre-exponential factor (frequency factor) E_a=activation energy, T=temperature

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

- **Activation energy :**
The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.
- Activation energy = threshold energy
  – average kinetic energy of reacting molecules
- Threshold energy = initial potential energy of reactant molecules + activation energy
- A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex which either breaks into products or reactants again.



(Exothermic) (Endothermic)

- Activation energy (E_a) = $E_{(\text{activated complex})} - E_{(\text{ground state})}$
  ΔH = activation energy of forward reaction
  – activation energy of backward reaction

Collision Theory

- Reactions occur when molecules collide with appropriate orientation and sufficient energy, not all molecular collisions result successfully in the formation of product.
- For any successful collision (one resulting in a reaction) :
  - particles must collide
  - they must collide with sufficient energy > E_a
  - they need to have correct alignment (collision geometry) (to keep E_a as low as possible)
- To account effective collision, another factor P, called orientation factor or steric factor or probability factor is introduced.

$$k = PZ_{AB}e^{-E_a/RT}$$

Thus, in collision theory, activation energy and proper orientation of the molecules determine the criteria for an effective collision and hence the rate of reaction.
Z_{AB} represents the collision frequency of reactant A and B.

EXAM DRILL

1. For $A + B \rightarrow C + D$, $\Delta H = -20$ kJ mol^{-1}. The activation energy of the forward reaction is 85 kJ mol^{-1}. The activation energy for backward reaction is .... kJ mol^{-1}.
(a) 65 (b) 105 (c) 85 (d) 40

2. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
(a) 1/2 g (b) 1/4 g (c) 1/8 g (d) 1/16 g

3. For the following endothermic reaction at a particular temperature, according to the equations,

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

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

the activation energies are E_1 and E_2 respectively, then
(a) $E_1 > E_2$ (b) $E_1 < E_2$
(c) $E_1 = 2E_2$ (d) $\sqrt{E_1E_2^2} = 1$

4. In the reaction, $A + 2B \longrightarrow C + 2D$, the initial rate $-d[A]/dt$ at $t = 0$ was found to be 2.6×10^{-2} M s^{-1}. What is the value of $-d[B]/dt$ at $t = 0$ in M s^{-1}?
(a) 2.6×10^{-2} (b) 5.2×10^{-2}
(c) 1.0×10^{-1} (d) 6.5×10^{-3}

5. The reaction mechanism for the reaction $P \rightarrow R$ is as follows:

$P \xrightarrow{k_1} Q$ (fast),

$Q + P \xrightarrow{k_2} R$ (slow)

The rate law for the main reaction $(P \rightarrow R)$ is
(a) $k_1[P][Q]$ (b) $k_1k_2[P]$
(c) $k_1k_2[P]^2$ (d) $k_1k_2[Q]$

6. The rate of reaction
$Cl_3CCHO + NO \rightarrow CHCl_3 + NO + CO$ is given by equation, Rate = $k[Cl_3CCHO][NO]$.
If concentration is expressed in mol/L, the units of k are
(a) L^2 mol^{-2} s^{-1} (b) Mol L^{-1} s^{-1}
(c) L mol^{-1} s^{-1} (d) s^{-1}

7. For a reaction $A + B \rightarrow$ products, it is found experimentally that the rate of the reaction $= k[A]^{1.5}[B]^{2.5}$. The order of the reaction is
(a) –1 (b) +1 (c) 3.75 (d) 4

8. In the reaction,
$CH_3COCH_{3(g)} \longrightarrow C_2H_{4(g)} + H_{2(g)} + CO_{(g)}$
the initial pressure is found to be 0.40 atm and after 10 min, it was 0.50 atm. The rate constant for first order reaction is [log4 = 0.6021, log3.5 = 0.5441]
(a) 0.0133 min^{-1} (b) 0.4 s^{-1}
(c) 10 s^{-1} (d) 0.6 min^{-1}

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

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

When a graph is plotted for log$k$ versus $1/T$ a straight line with a slope –5632 is obtained. The energy of activation for this reaction is
(a) 127.67 kJ mol^{-1} (b) 107.84 kJ mol^{-1}
(c) 86 kJ mol^{-1} (d) 246.8 kJ mol^{-1}.

10. For a reaction, $X \longrightarrow Y$, the graph of the product concentration (x) versus (t) came out to be a straight line passing through the origin. Hence the graph of $\frac{-d[X]}{dt}$ and time would be
(a) straight line with a negative slope and an intercept on y-axis
(b) straight line with a positive slope and an intercept on y-axis
(c) a straight line parallel to x-axis
(d) a hyperbola.

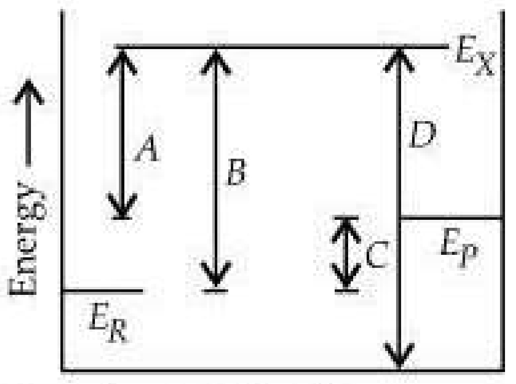
11. For the first order decomposition reaction of N_2O_5, it is observed that

(i) $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$; $-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$

(ii) $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$; $-\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$

Which of the following is true?
(a) $k = k'$ (b) $k = 2k'$ (c) $k = \frac{k'}{2}$ (d) $k = k'^2$

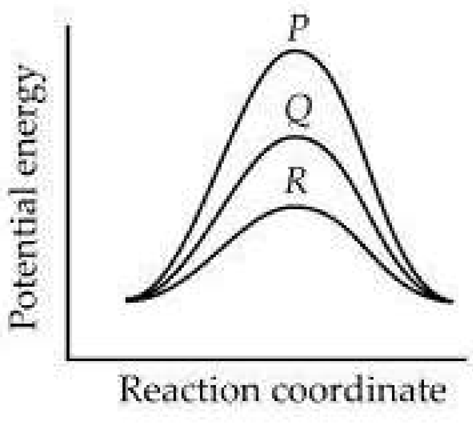
12. In the accompanied diagram, E_R, E_P and E_X represent the energy of the reactants, products and activated complex respectively. Which of the following is the activation energy for th e backward reaction?



(a) A (b) B (c) C (d) D

13. The rate constant of a reaction is 2.3×10^{-2} mol^{-2} L^2 min^{-1}. The order of reaction is
(a) zero (b) 1 (c) 2 (d) 3

14. If a homogeneous catalytic reaction can take place through three alternative paths as depicted below, the catalytic efficiency of P, Q, R representing the relative case would be



(a) $P > Q > R$ (b) $Q > P > R$
(c) $P > R > Q$ (d) $R > Q > P$

15. Which one of the following equation is correct for the reaction : $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$?

(a) $\frac{3d[H_2]}{dt} = \frac{2d[N_2]}{dt}$ (b) $\frac{2d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$

(c) $\frac{2d[NH_3]}{dt} = \frac{-3d[H_2]}{dt}$ (d) $\frac{3d[NH_3]}{dt} = \frac{-2d[H_2]}{dt}$

16. For a second order reaction in which both the reactants have equal initial concentration, the time taken for 20% completion of reaction is 500 second. What will be the time taken for 60% of the reaction?

(a) 500 sec (b) 1000 sec

(c) 3000 sec (d) 1500 sec

17. The reaction $A + B \rightarrow C + D + 40$ kJ has an activation energy of 18 kJ. Then the activation energy for the reaction $C + D \rightarrow A + B$ is

(a) 58 kJ (b) – 40 kJ

(c) –18 kJ (d) 22 kJ

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

(a) s^{-1} (b) mol L s^{-1}

(c) mol L^{-1} s^{-1} (d) no unit.

19. In a reaction, $2A + B \rightarrow A_2B$, the reactant B will disappear at

(a) half the rate as A will decrease

(b) the same rate as A will decrease

(c) twice the rate as A will decrease

(d) half the rate as A_2B will form.

20. Consider the reaction

$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

The rate law for this reaction is Rate = $k[N_2O_5]$

Which of the following statements is true regarding the above reaction?

(a) Its order is 1 and molecularity is 1.

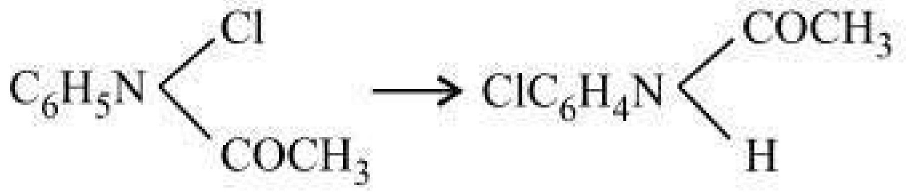
(b) Its order is 1 and molecularity is 2.

(c) Its order is 2 and molecularity is 2.

(d) Its order is 2 and molecularity is 1.

21. Which of the following given reaction(s) is/are of the first order?

I. $(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3COCH_3 + C_2H_6$

II. 
$C_6H_5N(Cl)(COCH_3) \longrightarrow ClC_6H_4N(COCH_3)(H)$

III. $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

IV. $RCOOR' + NaOH \longrightarrow RCOONa + R'OH$

(a) Only I and IV (b) Only I and II

(c) Only I and III (d) All of these.

22. For a pseudo first order reaction,

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

the net rate is given by

$$\frac{dx}{dt} = 4 \times 10^{-4}\ L\ mol^{-1}\ s^{-1}\ [(CH_3COOC_2H_5)] - 3 \times 10^4\ L\ mol^{-1}\ s^{-1}\ [CH_3COOH][C_2H_5OH]$$

Then, the equilibrium constant of the reaction would be

(a) 1.3×10^{-7} mol L^{-1} s^{-1}

(b) 1.3×10^{-6} mol L^{-1} s^{-1}

(c) 1.33×10^{-9} mol L^{-1}

(d) 1.33×10^{-8} mol L^{-1}

23. Consider following reactant sample

I. 1 mol of A and 1 mol of B in a 1 L vessel

II. 2 mol of A and 2 mol of B in a 2 L vessel

III. 0.2 mol of A and 0.2 mol of B in a 0.1 L vessel

Which of the reactant sample reacts at the highest rate?

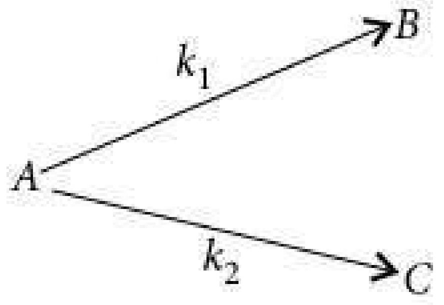
(a) I

(b) II

(c) III

(d) All are at equal rate.

24. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :

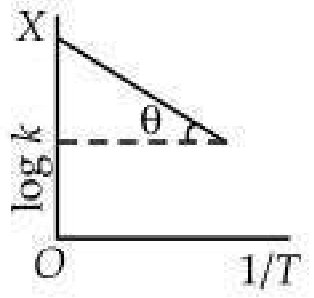


If $k_1 = 1.26 \times 10^{-4}\ s^{-1}$, $k_2 = 3.8 \times 10^{-5}\ s^{-1}$, then the percentage distributions of B and C are respectively

(a) 80%, 20% (b) 76.83%, 23.17%

(c) 90%, 10% (d) 63.94%, 36.06%

25. Graph between log k and $\frac{1}{T}$ is a straight line with $OX = 5$, $\tan\theta = \left(\frac{1}{2.303}\right)$. Hence, E_a will be



(a) 2.303×2 cal (b) $\frac{5}{2.303}$cal

(c) –2 cal (d) none of these.

26. How much faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?

(a) 2 times (b) 16 times

(c) 11 times (d) 6 times

27. The first order rate constant for the decomposition of ethyl iodide 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. Calculate the rate constant of the reaction at 700 K.

(a) $6.36 \times 10^{-3}\ s^{-1}$ (b) $6.24 \times 10^{-3}\ s^{-1}$

(c) $6.57 \times 10^{-3}\ s^{-1}$ (d) $6.86 \times 10^{-3}\ s^{-1}$

28. Which of the following statement(s) about the Arrhenius equation is incorrect?

(a) If $E_a = 0$, then $k = A$

(b) When the activation energy of the reaction is high, the rate becomes independent of temperature.

(c) Two reactions having same value of E_a do not necessarily have same rate.

(d) A reaction with higher value of E_a will have smaller value of rate constant.

29. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

(a) 2865 years (b) 1845 years

(c) 1765 years (d) 2345 years

30. If we doubled the initial concentration, for a certain first order chemical reaction, then $t_{1/2}$ for the reaction

(a) will increase by two times

(b) will decrease by four times

(c) remains same

(d) will decrease by half times.

31. For a first order reaction, $X \rightarrow$ Product, the initial concentration of X is 0.1 M and after 40 minutes it becomes 0.025 M. Calculate the rate of reaction at reactant concentration of 0.01 M.

(a) 3.47×10^{-4} M min^{-1} (b) 3.47×10^{-5} M min^{-1}

(c) 1.735×10^{-6} M min^{-1} (d) 1.735×10^{-4} M min^{-1}

32. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A.e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting which of the following

(a) k vs T (b) k vs $\frac{1}{\log T}$

(c) $\log k$ vs $\frac{1}{T}$ (d) $\log k$ vs $\frac{1}{\log T}$

33. Unit of rate constant 'k' for the second order reaction is

(a) mol^{-1} L^{-1} s^{-1} (b) mol^{-1} L s^{-1}

(c) mol L^{-1} s^{-1} (d) mol L^{-1} s

34. In a first order reaction, $R \rightarrow Q$, if 'k' is the rate constant and initial concentration of the reactant R is 0.5 M, then the half-life is

(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5\,k}$

35. Which one of the following statements for the order of a reaction is incorrect?

(a) Order can be determined only experimentally.

(b) Order is not influenced by stoichiometric coefficient of the reactants.

(c) Order of a reaction is sum of power to the concentration terms of reactants to express the rate of reaction.

(d) Order of reaction is always whole number.

36. In most cases, for a rise of 10 K temperature the rate constant is doubled. This is due to the reason that

(a) collision frequency increases by a factor of 2 to 3

(b) fraction of molecules possessing threshold energy increases by a factor of 2 to 3

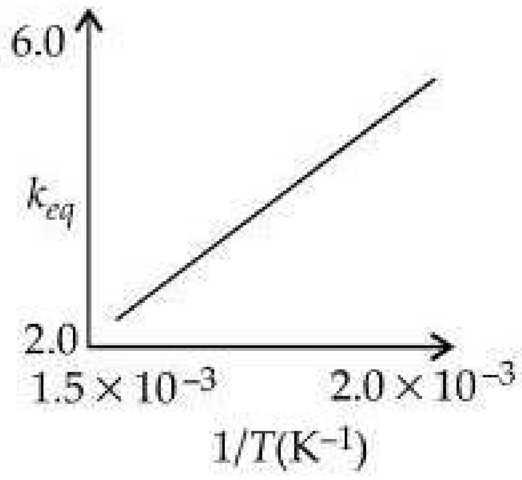
(c) activation energy is lowered by a factor of 2 to 3

(d) none of these.

37. A first order reaction has $k = 1.5 \times 10^{-2}$ s^{-1} at 100°C and the reaction is allowed to take place for 10 min. What is the final concentration of reactants if initial concentration is 100 moles?

(a) 10^{-7} (b) 10^{-5} (c) 10^{-6} (d) 10^{-2}

38. A schematic plot of $\ln k_{eq}$ versus inverse of temperature for a reaction is shown in the figure. The reaction must be



(a) exothermic

(b) endothermic

(c) one with negligible enthalpy change

(d) highly spontaneous at ordinary temperature.

39. The rate law for the reaction

$xA + yB \longrightarrow mP + nQ$ is Rate $= k\,[A]^c[B]^d$.

What is the total order of the reaction?

(a) $(x + y)$ (b) $(m + n)$

(c) $(c + d)$ (d) x/y

40. For a first order reaction, the time taken to reduce the initial concentration by a factor of 1/4 is 20 minutes. The time required to reduce initial concentration by a factor of 1/16 is

(a) 20 min (b) 10 min

(c) 80 min (d) 40 min

41. A catalyst

(a) increases the average kinetic energy of the reacting molecules

(b) decreases the activation energy

(c) increases the frequency of collision of the reacting species

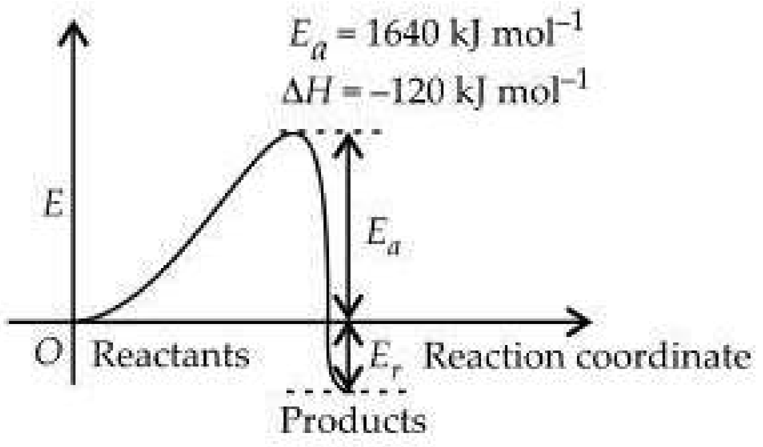
(d) alters the reaction mechanism

42. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate of reaction is

(a) $\frac{1}{2}\frac{d}{dt}[N_2O_5]$ (b) $2\frac{d}{dt}[N_2O_5]$

(c) $\frac{1}{4}\frac{d}{dt}[NO_2]$ (d) $4\frac{d}{dt}[NO_2]$

43. From the above figure, the activation energy for the reverse reaction would be



(a) − 120 kJ mol^{-1}
(b) + 152 kJ mol^{-1}
(c) + 120 kJ mol^{-1}
(d) + 1760 kJ mol^{-1}

44. The rate of a chemical reaction doubles for every 10° rise in temperature. If the temperature is increased by 60°C, the rate of reaction increases by about

(a) 20 times (b) 32 times
(c) 64 times (d) 128 times.

45. Match the plots given in List I with their slopes given in List II and select the correct answer using the code given below the lists :

	List I	**List II**
P.	C *vs* t (abscissa) for zero order reaction	1. Unity
Q.	log C *vs* t (abscissa) for first order reaction	2. Zero
R.	$\left(-\dfrac{dC}{dt}\right)$ *vs* C for zero order reaction	3. $-k$
S.	$\ln\left(-\dfrac{dC}{dt}\right)$ *vs* ln C for first order reaction	4. $-\dfrac{k}{2.303}$

	P	**Q**	**R**	**S**
(a)	4	3	2	1
(b)	3	4	2	1
(c)	2	4	3	1
(d)	3	2	4	1

DAY 18 OMR SHEET

Time : 45 min

INSTRUCTIONS

- Use HB pencil only and darken each circle completely.
- If you wish to change your answer, erase the already darkened circle completely and then darken the appropriate circle.
- Mark only one choice for each question as indicated.

Correct marking ● ⓑ ⓒ ⓓ

Wrong marking ⊗ ⓑ ◐ ⊙

1. ⓐ ⓑ ⓒ ⓓ
2. ⓐ ⓑ ⓒ ⓓ
3. ⓐ ⓑ ⓒ ⓓ
4. ⓐ ⓑ ⓒ ⓓ
5. ⓐ ⓑ ⓒ ⓓ
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7. ⓐ ⓑ ⓒ ⓓ
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43. ⓐ ⓑ ⓒ ⓓ
44. ⓐ ⓑ ⓒ ⓓ
45. ⓐ ⓑ ⓒ ⓓ

(1) Number of questions attempted : ____________

(2) Number of questions correct : ____________

(3) Marks scored : ___________

For every correct answer award yourself 4 marks. For every incorrect answer deduct 1 mark.

HINTS & SOLUTIONS

1. **(b)** : For a reaction, E_a for forward reaction = E_a for backward reaction + ΔH

$\therefore \quad 85 = E_{a(\text{back})} - 20 \quad \text{or} \quad E_{a(\text{back})} = 105 \text{ kJ mol}^{-1}$

2. **(d)** : Since $T = n \times t_{1/2}$

$560 = n \times 140\ ;\ n = 4$

Now, $\frac{[A]}{[A]_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

Given, $[A]_0 = 1$

$\frac{[A]}{1} = \frac{1}{16} \quad \Rightarrow \quad [A] = \frac{1}{16}\text{ g}$

3. **(a)**

4. **(b)** : $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$

Therefore, $-\frac{d[B]}{dt} = 2 \times \frac{-d[A]}{dt}$

$= 2 \times 2.6 \times 10^{-2} \text{ M s}^{-1} = 5.2 \times 10^{-2} \text{ M s}^{-1}$

5. **(c)** : As the slowest step is the rate determining step hence from eqn (ii)

rate = $k_2[P][Q]$ ...(iii)

From eqn (i) $k_1 = \frac{[Q]}{[P]}$ or $[Q] = k_1[P]$

Substituting the value in eqn (iii) we get,

rate = $k_1k_2[P]^2$

6. **(c)** : $\frac{dx}{dt} = k\ (\text{Conc.})^2$

or $k = \frac{\text{Conc.}}{\text{Time}} \times \frac{1}{(\text{Conc.})^2} = \text{Conc.}^{-1}\ \text{time}^{-1} = \text{L mol}^{-1}\text{ s}^{-1}$

7. **(d)** : The order of reaction is the sum of the powers to which molar concentration terms are raised in the rate law.

Therefore, order = 1.5 + 2.5 = 4

8. **(a)** : $CH_3COOCH_{3(l)} \longrightarrow C_2H_{4(g)} + H_{2(g)} + CO_{(g)}$

$$\begin{array}{cccc} 0.4 & 0 & 0 & 0 \\ 0.4 - x & x & x & x \end{array}$$

$0.4 - x + x + x + x = 0.50$

$\Rightarrow \quad 2x = 0.10 \quad \Rightarrow \quad x = 0.05$

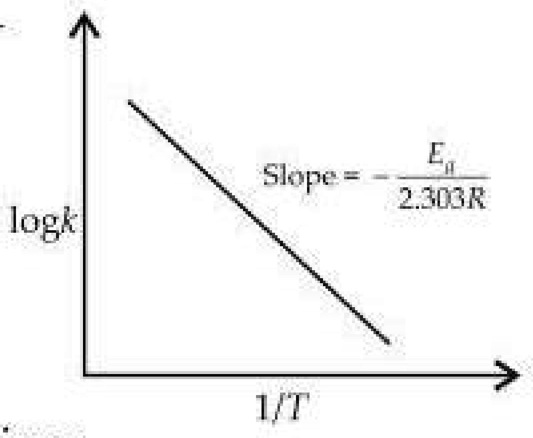
$$k = \frac{2.303}{10}\log\frac{0.4}{0.4-0.05} = \frac{2.303}{10}\log\frac{0.40}{0.35}$$

$$= \frac{2.303}{10}\log\frac{40}{35} = \frac{2.303}{10}[1.6021 - 1.5441]$$

$$= \frac{2.303}{10} \times 0.0580 = \frac{0.1335}{10} = 0.01335 \text{ min}^{-1}$$

$$= 0.01335 \times 60 = 0.8 \text{ s}^{-1}$$

9. **(b)** : $\log k = \text{constant} - \frac{E_a}{2.303RT}$



$-\frac{E_a}{2.303R} = -5632$

$E_a = 5632 \times 2.303 \times 8.314 = 107836$

$E_a \approx 107.836 \text{ kJ mol}^{-1}$.

10. **(c)** : If product concentration is x,

for a zero order reaction, $\frac{x}{t} = k$

Thus graph of x *vs* t would be a straight line passing through origin.

So, the given information is for zero order reaction.

For a zero order reaction, rate of the reaction is constant. Thus plot of rate *vs* time,

i.e., $\frac{-d[X]}{dt}$ *vs* time will be a straight line parallel to x-axis.

11. **(b)** : For the reaction :

$N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$

Rate = $-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$

For the reaction,

$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

Rate = $-\frac{1}{2}\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$

Since $-\frac{d[N_2O_5]}{dt}$ does not depend upon the way the chemical reaction is formulated, therefore

$-\frac{d[N_2O_5]}{dt} = 2k'[N_2O_5] = k[N_2O_5] \Rightarrow k = 2k'$

12. **(a)** : For backward reaction, activation energy is the energy difference between product and activated complex.

13. **(d)** : Unit of rate constant = $\left(\frac{\text{litre}}{\text{mol}}\right)^{n-1}\text{sec}^{-1}$

If $n = 3$, then $\text{mol}^{-2}\ \text{litre}^2\ \text{sec}^{-1}$

From the units, it is clear that the order of reaction is three.

14. **(d)** : The catalytic efficiency of a catalyst is measured in terms of the decrease in activation energy of the reaction. A catalyst is more efficient if it decreases the E_{act} to a larger extent. Thus correct order for catalytic efficiency is $R > Q > P$.

15. **(d)** : $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$-\frac{d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

$\therefore \quad 3\frac{d[NH_3]}{dt} = -2\frac{d[H_2]}{dt}$

16. (c) : We know that $k = \frac{1}{t} \times \frac{x}{a(a-x)}$

[For a second order reaction]

Since $x = \frac{20}{100} = 0.2, \quad a = 1$

$$k = \frac{1 \times 0.2}{500 \times 1(1-0.2)} = \frac{1}{500 \times 4}$$

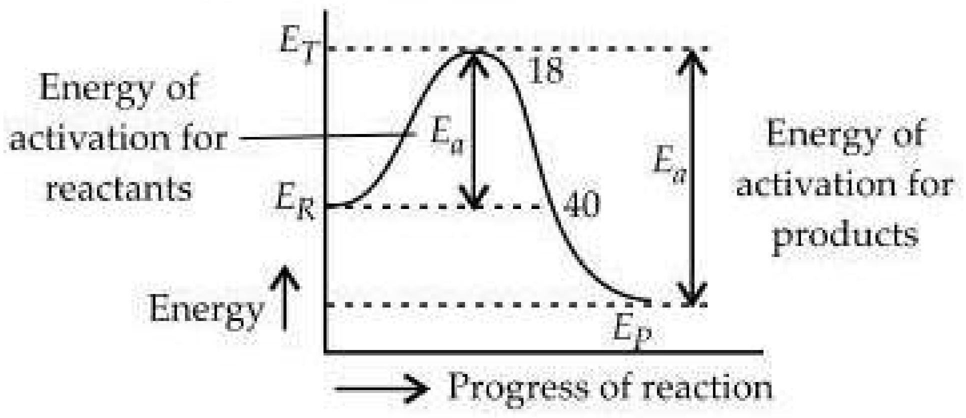
Now, $k = \frac{1}{t} \times \frac{0.6}{1(1-0.6)}$

$\therefore \quad \frac{1}{500 \times 4} = \frac{1}{t} \times \frac{0.6}{0.4} \Rightarrow t = 3000$ seconds

17. (a) : The minimum amount of energy absorbed by the reactants so that their energy becomes equal to threshold energy is called activation energy.

For the products activation energy will be

40 + 18 = 58 kJ.



18. (c) : Unit of rate constant for a zero order reaction,

$k = \frac{x}{t} = \text{mol L}^{-1}\ \text{s}^{-1}$

19. (a) : $2A + B \longrightarrow A_2B$

The rate of disappearance of reactant will be

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[A_2B]}{dt}$$

20. (b) : From the rate law, order of the reaction is 1. From the reaction equation, molecularity is 2.

21. (b) **22. (d)**

23. (c) : Vessel III has highest concentration of reactants,

$c = \frac{n}{V} = \frac{0.2}{0.1} = 2$ mol/L (for each reactant)

Higher the concentration of reactants higher is the rate of reaction.

24. (b) : For parallel path reaction,

$k_{\text{average}} = k_1 + k_2 = 1.26 \times 10^{-4} + 3.8 \times 10^{-5} = 1.64 \times 10^{-4}\ \text{s}^{-1}$

Fractional yield of $B = \frac{k_1}{k_{\text{average}}} = \frac{1.26 \times 10^{-4}}{1.64 \times 10^{-4}} = 0.7683$

Percentage distribution of $B = 76.83\%$

Fractional yield of $C = \frac{k_2}{k_{\text{average}}} = \frac{3.8 \times 10^{-5}}{1.64 \times 10^{-4}} = 0.2317$

Percentage distribution of $C = 23.17\%$

25. (c) : $\log k = \log A - \frac{E_a}{2.303RT}$

$\text{Slope} = \frac{-E_a}{2.303R} = \frac{1}{2.303}$(given)

$E_a = -2.303\ R \times \text{slope} = R = -2$ cal

26. (c) : $2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right];$

$$\therefore \quad 2.303 \log \frac{k_2}{k_1} = \frac{65 \times 10^3}{8.314}\left[\frac{298-273}{298 \times 273}\right]$$

$$\therefore \quad \frac{k_2}{k_1} = 11.04 \simeq 11$$

27. (a) : We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$\log k_2 - \log (1.60 \times 10^{-5})$

$$= \frac{209000\text{J mol L}^{-1}}{2.303 \times 8.314\,\text{J mol L}^{-1}\text{K}^{-1}}\left[\frac{1}{600\text{ K}} - \frac{1}{700\text{ K}}\right]$$

$\log k_2 = -4.796 + 2.599 = -2.197$

$k_2 = 6.36 \times 10^{-3}\ \text{s}^{-1}$

28. (b)

29. (b) : The rate constant is given by

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}\text{years}^{-1}$$

It is known that

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303 \times 5730}{0.693}\log\frac{100}{80}$$

= 1845 years (approx.)

30. (c) : $t_{1/2}$ for first order reaction $= \frac{0.693}{k}$

Therefore, $t_{1/2}$ is independent of initial concentration.

31. (a) : $k = \frac{2.303}{40}\log\frac{0.1}{0.025} \Rightarrow k = 0.03466\ \text{min}^{-1}$

Rate $= k \times 0.01 = 0.03466 \times 0.01 = 3.47 \times 10^{-4}\ \text{M min}^{-1}$

32. (c) : On plotting log *k vs* 1/*T*, we get a straight line, the slope indicates the value of activation energy.

33. (b) : $k = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$

For second order, $n = 2$

$$k = \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\ \text{L s}^{-1}$$

34. (c) : For a first order reaction,

$$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}\text{ ; when } t = t_{1/2},\ x = 0.5/2$$

$$\therefore\quad k = \frac{2.303}{t_{1/2}}\log_{10}\frac{0.5}{0.5-(0.5/2)}$$

$$\Rightarrow\quad t_{1/2} = \frac{2.303}{k}\log_{10}2 = \frac{\ln 2}{k}$$

35. (d) : Order of a reaction is not always whole number. It can be zero, or fractional also.

36. (b) : For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

37. (d) : $k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} \Rightarrow 1.5\times10^{-2} = \frac{2.303}{10\times60}\log\frac{100}{[A]}$

$$\log\frac{100}{[A]} = \frac{1.5\times10^{-2}\times600}{2.303} \approx 4$$

$$\frac{100}{[A]} = 10^4;\ [A] = \frac{100}{10^4} = 10^{-2}\ \text{mol L}^{-1}$$

38. (a) : $\ln\frac{k_2}{k_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$

$$\ln\frac{6}{2} = \frac{\Delta H}{R}\left[1.5\times10^{-3}-2\times10^{-3}\right]$$

ΔH comes to be negative. Hence the reaction is exothermic.

39. (c) : Order is the sum of the powers to which the concentration terms are raised in the rate equation.

40. (d) : $1 \xrightarrow{1^{\text{st}}} 1/2 \xrightarrow{2^{\text{nd}}} 1/4 \xrightarrow{3^{\text{rd}}} 1/8 \xrightarrow{4^{\text{th}}} 1/16$

1/16 is 4 half-lives and 1/4 is 2 half-lives. It is given that the time taken for 2 half-lives is 20 minutes. So the time taken for half-lives will be 40 minutes.

41. (c) : A catalyst lowers the activation energy barrier and this alters the reaction mechanism.

42. (c) : For $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[0]}{dt}$$

43. (d) : Given $\Delta H = -120$ kJ mol^{-1}; $E_a = 1640$ kJ mol^{-1}

For reverse reaction, $\Delta H = +120$ kJ mol^{-1}

$\therefore$ Activation energy for the reverse reaction
$= 1640 + 120 = +1760$ kJ mol^{-1}

44. (c) : Since for every 10° rise in temperature, rate increases by two times therefore for 60° rise in temperature the rate will increase $2^6 = 64$ times.

45. (b) : (P) For a zero order reaction, $C = C_0 - kt$

(Q) For a first order reaction, $\log C = \log C_0 - \frac{k}{2.303}\times t$

(R) For a zero order reaction, $-\frac{dC}{dt} = k$ (constant)

Hence, slope of $-\frac{dC}{dt}\ vs\ C = 0$

(S) For a first order reaction, $-\frac{dC}{dt} = kC,$

$$\ln\left(-\frac{dC}{dt}\right) = \ln k + \ln C.$$

Hence, plot of $\ln\left(-\frac{dC}{dt}\right)$ against $\ln C$ will have slope equal to unity.