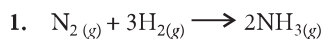


Detailed Solutions



$$\frac{-d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

2. **Elementary step** : Each step of a complex reaction is called an elementary step.

3. The rate of a reaction does not remain constant throughout the reaction process because the rate of the reaction depends upon concentration of reactants which keeps on decreasing.

4. Change in concentration *i.e.*, either (decrease in concentration of reactant or increase in concentration of product) per unit time is called rate of reaction.

$$\text{Rate of reaction} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{\Delta C}{\Delta t}$$

The ratio of change of concentration of reactants to the time consumed in that change is called average rate of reaction.

$$r_{av} = \frac{\Delta x}{\Delta t} = -\frac{C_2 - C_1}{t_2 - t_1}$$

The rate of reaction at a particular instant (time) is called instantaneous rate of reaction.

$$r_{ins} = \frac{dx}{dt}$$

dx = small change in concentration

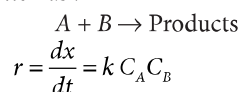
dt = small time interval

5. Refer to answer 4.

6. Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

7. At a given temperature, rate is equal to the rate constant of reaction when concentration of the reactant is unity. Thus rate constant is also known as specific reaction rate.

In the case of two reactants, the reaction may be written as :



where all the terms have their usual meaning as :

if $C_A = C_B = 1$ then $r = k$.

8. $A + B \rightarrow \text{Product}$

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

Order of reaction is sum of the powers of concentration terms,

$$\therefore \text{Order of reaction} = \frac{1}{2} + 2 = \frac{5}{2} = 2.5$$

9. First order reaction.

10. It is defined as "the sum of the powers or exponents to which the concentration terms are raised in the rate law expression."

If rate = $k[A]^m [B]^n$, then order = $m + n$.

11. Second order reaction :

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

12. Distinction between order and molecularity of a reaction : (any one)

| Order of a reaction | Molecularity of a reaction |
|--|---|
| 1. It is the sum of powers of the concentration of the reactants in the rate law expression. | 1. It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction. |
| 2. It need not be a whole number. | 2. It is always a whole number. |

Generally, in a complex reaction the order of reaction is equal to the molecularity of the slowest step.

13. Refer to answer 10.

14. Rate = $k[\text{Cl}_2] [\text{NO}]^2$

Hence order of the reaction = $1 + 2 = 3$

15. Rate = $\frac{-1}{3} \frac{d[\text{H}_2]}{dt}$

16. (i) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

In this reaction, platinum metal acts as a catalyst.

At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

However, two molecules of ammonia react to give products thus, the molecularity is two.

(ii) For a zero order reaction, unit of rate constant is $\text{mol L}^{-1} \text{sec}^{-1}$.

17. (i) Rate = k

Experimentally, it is found that the rate of reaction is independent of the concentration of H_2 and Cl_2 . Hence, it is a zero order reaction.

Molecularity = 2

(ii) Unit of k = mole litre⁻¹ sec⁻¹

18. (i) From the rate law equation, order of reaction w.r.t. B is 2. Hence, if concentration of B is doubled, rate will become four times.

(ii) If A is present in large excess, rate of reaction will be independent of concentration of A and hence, order of reaction will be 2.

19. Refer to answer 4.

Following factors affect the rate of a chemical reaction :

(i) **Concentration of reactants** : Higher the concentration of reactants, faster would be the rate of reaction.

Rate = $k C^n$, where C = concentration of reactant.

(ii) **Temperature** : The rate of reaction increases with the temperature. For every 10°C rise in temperature rate of reaction increases 2 to 3 times.

20. Unit of rate constant (k), for zero order reaction.

$$\text{Rate} = k[A]^0 \Rightarrow k = \text{mol L}^{-1} \text{s}^{-1}$$

Unit of rate constant (k), for second order reaction

$$\text{Rate} = k[A]^2 \Rightarrow k = \text{mol}^{-1} \text{L s}^{-1}$$

21. Refer to answer 12.

22. (i) Order of reaction is sum of powers of concentration terms,

$$\therefore \text{Order of reaction} = 1 + 2 = 3$$

(ii) Refer to answer 28.

23. Let the concentration of the reactant $[A] = a$

Order of reaction = 2 so that

$$\begin{aligned} \text{Rate of reaction} &= k[A]^2 \\ &= ka^2 \end{aligned} \quad \dots(1)$$

(i) Given that concentration of the reactant is doubled So, that $[A] = 2a$,

Putting the value in equation (1) we get

$$\text{New rate of reaction, } R_1 = k(2a)^2 = 4ka^2$$

Hence, rate of reaction will increase to 4 times.

(ii) Given that concentration of the reactant is reduced to half

$$\text{So that } [A] = (1/2)a$$

Putting the value in equation (1), we get

$$\begin{aligned} \text{New rate of reaction } R_2 &= k((1/2)a)^2 \\ &= (1/4)ka^2 \end{aligned}$$

Hence, rate of reaction will reduce to 1/4.

24. **Order of a reaction** : Refer to answer 10.

(i) $\text{L}^{-1} \text{mol s}^{-1}$ – Zero order reaction

(ii) $\text{L mol}^{-1} \text{s}^{-1}$ – Second order reaction

25. Rate expression is a way of expressing rate of reaction in terms of concentration of reactants, e.g., for a general reaction, $aA + bB \rightarrow cC + dD$

$$\text{Rate} = k[A]^x [B]^y$$

Rate constant (k) is equal to the rate of reaction when molar concentration of reactant is unity. Its units depend upon the order of reaction.

26. Refer to answers 25 and 24.

27. Refer to answer 25.

28. **Order of a reaction** : Refer to answer 10.

Unit for first order rate constant :

For first order reaction,

$$\text{Rate} = \frac{dx}{dt} = k[A]$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k \cdot \text{mol L}^{-1} \Rightarrow k = \frac{1}{\text{sec}} = \text{sec}^{-1}$$

29. Refer to answer 6.

Unit for k :

(i) For a zero order reaction : $\text{mol L}^{-1} \text{s}^{-1}$

(ii) For a first order reaction : s^{-1} .

30. Factors affecting the rate of a chemical reaction :

(i) **Concentration of reactants** : In general the rate of a reaction increases when concentration of reactants is increased.

$$\text{Rate} = kC^n$$

(ii) **Temperature** : Most of the chemical reactions are accelerated by increase in temperature.

(iii) **Catalyst** : Rate of a reaction increases in presence of a catalyst.

(iv) **Nature of reactants** : Reactions involving ionic reactants are fast as compared to those involving covalent reactants.

(v) **Surface area of the reactants** : In case of solid reactants, the rate of reaction increases with the surface area of the particles of the reactants.

(vi) **Light** : In case of photochemical reactions, the rate of reaction increases with increasing the intensity of light.

31. Refer to answer 12.

32. Since the reaction is second order in A and first order in B

(i) Differential rate equation is

$$\text{Rate} = k[A]^2[B]$$

(ii) The new concentration of A = [3A]

$$\therefore \text{New rate} = k[3A]^2[B] = 9k[A]^2[B]$$

\therefore New rate = 9 times of the original rate

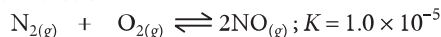
(iii) New concentration of A = [2A]

New concentration of B = [2B]

$$\therefore \text{New rate} = k[2A]^2[2B] = 8k[A]^2[B]$$

\therefore New rate = 8 times of the original rate.

33. Given reaction is



Initially: 0.80 mol L⁻¹ 0.20 mol L⁻¹ 0

At equil.: 0.80 - x 0.20 - x 2x

According to law of mass action,

$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$\text{or } 1.0 \times 10^{-5} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)}$$

x is very small hence can be neglected in the denominator. Thus,

$$1.0 \times 10^{-5} = \frac{4x^2}{0.8 \times 0.2} \text{ or } 1.0 \times 10^{-5} = \frac{4x^2}{0.16}$$

$$\text{or, } 4x^2 = 1.0 \times 10^{-5} \times 0.16 \text{ or } 4x^2 = 16 \times 10^{-7}$$

$$\text{or, } x^2 = 4 \times 10^{-7} \text{ or } x = 6.32 \times 10^{-4}$$

$$\therefore [\text{N}_2] = 0.80 - 0.000632 = 0.7994 \text{ mol L}^{-1}$$

$$[\text{O}_2] = 0.20 - 0.000632 = 0.199 \text{ mol L}^{-1}$$

$$[\text{NO}] = 2x = 2 \times 0.000632 = 0.001264 \text{ mol L}^{-1}$$

34. (i) (a) Differential rate equation of reaction is

$$\frac{dx}{dt} = k[A]^1[B]^2 = k[A][B]^2$$

When conc. of B is tripled, it means conc. of B becomes [3 × B]

$$\therefore \text{New rate of reaction, } \frac{dx'}{dt} = k[A][3B]^2$$

$$= 9k[A][B]^2 = 9 \left(\frac{dx}{dt} \right)$$

i.e., the rate of reaction will become 9 times.

(i) When conc. of A is doubled and that of B is also doubled, then conc. of A becomes [2A] and that of B becomes [2B].

$$\therefore \text{Now rate of reaction, } \frac{dx'}{dt} = k[2A][2B]^2 = 8k[A][B]^2$$

i.e., the rate of reaction will become 8 times.

(ii) **Molecularity of a reaction is the number of reacting particles which collide simultaneously to bring about the chemical change. It is a theoretical concept.**

$$35. (i) \text{Rate} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{2} \times 1 \times 10^{-2}$$

$$= 0.5 \times 10^{-2} \text{ mol/L/s.}$$

$$(ii) \text{Rate} = \frac{-d[A]}{dt} = \frac{-1}{2} \frac{d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt}$$

Rate of change in concentration of A,

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

$$= 0.5 \times 10^{-2} \text{ mol/L/s.}$$

Rate of change in concentration of C,

$$= +\frac{d[C]}{dt} = -\frac{3}{2} \frac{d[B]}{dt} = \frac{3}{2} \times 10^{-2}$$

$$= 1.5 \times 10^{-2} \text{ mol/L/s.}$$

36. (i) Let rate law for the disappearance of N₂O₅ is

$$\text{Rate} = k[\text{N}_2\text{O}_5]^a$$

$$\text{Then } \frac{r_1}{r_2} = \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{k(1.13 \times 10^{-2})^a}{k(0.84 \times 10^{-2})^a}$$

$$\text{or, } \frac{34}{25} = \left(\frac{113}{84} \right)^a \text{ or } a = 1$$

Thus, order of reaction = 1

$$(ii) r = k[\text{N}_2\text{O}_5] \text{ or, } 34 \times 10^{-5} = k \times 1.13 \times 10^{-2}$$

$$\text{or, } k = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 3.0 \times 10^{-2} \text{ min}^{-1}$$

(iii) Rate law = k[N₂O₅]

37. The reaction is



Here : $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

The order of reaction is 0 i.e.,

$$\text{Rate} = k [\text{Reactant}]^0$$

$$\text{Rate} = 2.5 \times 10^{-4} \times 1 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of reaction} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

The rate of formation of $\text{N}_2 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\text{Again, } 2.5 \times 10^{-4} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\therefore \frac{d[\text{H}_2]}{dt} = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Therefore, rate of formation of H_2
 $= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

38. Suppose order with respect to A is m and with respect to B is n . Then the rate law will be

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

Substituting the value of experiments 1 to 4, we get

$$\text{Expt. 1 : Rate} = 6.0 \times 10^{-3} = k(0.1)^m(0.1)^n \quad \dots(\text{i})$$

$$\text{Expt. 2 : Rate} = 7.2 \times 10^{-2} = k(0.3)^m(0.2)^n \quad \dots(\text{ii})$$

$$\text{Expt. 3 : Rate} = 2.88 \times 10^{-1} = k(0.3)^m(0.4)^n \quad \dots(\text{iii})$$

$$\text{Expt. 4 : Rate} = 2.4 \times 10^{-2} = k(0.4)^m(0.1)^n \quad \dots(\text{iv})$$

Comparing equation (i) and equation (iv),

$$\therefore \frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k(0.1)^m(0.1)^n}{k(0.4)^m(0.1)^n}$$

$$\text{or, } \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m \therefore m = 1$$

Comparing equation (ii) and equation (iii)

$$\frac{(\text{Rate})_2}{(\text{Rate})_3} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k(0.3)^m(0.2)^n}{k(0.3)^m(0.4)^n}$$

$$\text{or, } \left(\frac{1}{2}\right)^2 = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n \therefore n = 2$$

$$\therefore \text{Rate law expression is : Rate} = k[\text{A}][\text{B}]^2$$

The rate constant can be calculated from the given data of any experiment using expression :

$$k = \frac{\text{Rate}}{[\text{A}][\text{B}]^2}$$

$$\text{From Expt. 1, } k = \frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$$

$$\therefore \text{Rate constant } k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

$$\text{Unit of } k, \frac{dx}{dt} = k[\text{A}]^1[\text{B}]^2 = 6.0[0.5][0.2]^2$$

$$= 6 \times 5 \times 4 \times 10^{-3} \\ = 1.2 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}$$

39. The time taken for half of the reaction to complete, i.e., the time in which the concentration of a reactant is reduced to half of its original value

Is called half-life period of the reaction.

$$t = t_{1/2} \text{ when } [\text{R}] = \frac{[\text{R}_0]}{2}$$

$$40. \text{ For a first order reaction, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{x}$$

For $\frac{3}{4}$ th life period, $a = a$

$$a - x = a - \frac{3}{4}a = \frac{1}{4}a$$

$$\therefore k = \frac{2.303}{y} \log \frac{a}{(a-x)}$$

$$\frac{0.693}{x} = \frac{2.303}{y} \log \frac{a}{a/4}$$

$$\frac{0.693}{x} = \frac{2.303}{y} 2 \log 2$$

$$\frac{0.693}{x} = \frac{0.693 \times 2}{y}$$

$$y = 2x$$

41. (i) The reaction is of zero order.
 (ii) Slope of the straight line graph gives 'k'

$$= -k = \frac{d[\text{R}]}{dt}$$

42. Refer to answer 39.

(i) For zero order reaction rate constant is given by :

$$k = \frac{[\text{R}]_0 - [\text{R}]}{t}, \text{ At } t = t_{1/2}, [\text{R}] = \frac{[\text{R}]_0}{2}$$

$$k = \frac{[\text{R}]_0 - \frac{[\text{R}]_0}{2}}{t_{1/2}} \Rightarrow k = \frac{[\text{R}]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \frac{[\text{R}]_0}{2k}$$

In zero order reaction, $t_{1/2}$ is directly proportional to $[\text{R}]_0$.

(ii) For first order reaction,

$$k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]}, \text{ At } t = t_{1/2}, [\text{R}] = \frac{[\text{R}]_0}{2}$$

$$\therefore k = \frac{2.303}{t_{1/2}} \log \frac{[\text{R}]_0}{[\text{R}]_0/2} \text{ or, } t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \frac{0.693}{k}$$

In first order reaction, $t_{1/2}$ is independent of initial concentration.

43. For first order reaction, $t = \frac{2.303}{k} \log \frac{[R_0]}{[R_t]}$

For 99% completion of reaction

$$t = t_{0.99}, [R]_0 = 1, [R]_t = (1 - 0.99) = 0.01 = 10^{-2}$$

$$t_{0.99} = \frac{2.303}{k} \log \frac{1}{10^{-2}} = \frac{2.303}{k} \log 10^2 = \frac{2.303}{k} \times 2 \quad \dots(i)$$

For 90% completion of reaction

$$t = t_{0.90}, [R]_0 = 1, [R]_t = (1 - 0.9) = 0.1 = 10^{-1}$$

$$t_{0.90} = \frac{2.303}{k} \log \frac{1}{10^{-1}} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \quad \dots(ii)$$

Comparing equations (i) and (ii),

$$t_{0.99} = 2 \times t_{0.90}$$

44. The integrated rate equation for first order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{a}{a - \frac{3}{4}a}$$

$$k = \frac{2.303}{t} \log \frac{a}{0.25a}$$

$$t_{3/4} = \frac{2.303}{2.54 \times 10^{-3} \text{ sec}^{-1}} \times \log \frac{1}{0.25}$$

$$t_{3/4} = 546 \text{ s}$$

Therefore, the 3/4th life of the reaction is 546 seconds.

45. For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

Given $k = 2.4 \times 10^{-3} \text{ s}^{-1}$

$$[R] = \frac{[R]_0}{4}, t = ?$$

Substituting these values in the equation, we get

$$t = \frac{2.303}{2.4 \times 10^{-3} \text{ s}^{-1}} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{2.4 \times 10^{-3} \text{ s}^{-1}} \log 4 = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021 \text{ s}$$

$$t = 577.7 \text{ s} = 578 \text{ s}$$

46. $a = 0.6 \text{ mol/L}$, $(a - x) = 0.4 \text{ mol/L}$

$$t = 5 \text{ min}$$

$$k = \frac{2.303}{5 \text{ min}} \log \frac{0.6}{0.4} = 0.0811 \text{ min}^{-1}$$

47. Refer to answer 42(ii).

48. Here $t = 40 \text{ min}$, $t_{1/2} = ?$

Let $a = 100$ $\therefore x = 30\%$ of $100 = 30$

Using the formula,

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\Rightarrow 40 = \frac{2.303}{k} \log \frac{100}{100-30}$$

$$40 = \frac{2.303}{k} \log \frac{100}{70}$$

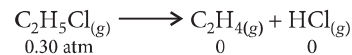
$$\Rightarrow 40 = \frac{2.303}{k} (\log 10 - \log 7)$$

$$40 = \frac{2.303}{k} (1 - 0.8451)$$

$$\Rightarrow 40 = \frac{2.303}{k} \times 0.1549 \Rightarrow k = \frac{0.357}{40} = 0.0089 \text{ min}^{-1}$$

$$\therefore t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0089} = 77.86 \text{ min.}$$

49. The given reaction is



At time $t = 0$



At time $t = 300 \text{ sec}$



Total pressure = $0.30 - x + x + x = 0.50$

or $0.30 + x = 0.50$

$$\therefore x = 0.50 - 0.30 = 0.20$$

$$\therefore \text{Initial pressure, } P_0 = 0.30 \text{ atm}$$

Pressure of $\text{C}_2\text{H}_5\text{Cl}$ after 300 sec, $P_t = 0.30 - 0.20 = 0.10 \text{ atm}$

Using formula for first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_t}$$

$$k = \frac{2.303}{300} \log \frac{0.30}{0.10}$$

$$k = \frac{2.303}{300} \log 3 = \frac{2.303 \times 0.4771}{300} = 3.66 \times 10^{-3} \text{ sec}^{-1}$$

50. $t_{50\%}$ or $t_{1/2} = 30 \text{ minutes}$

$$\Rightarrow k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100-90} = \frac{2.303}{0.0231} \log 10$$

$$= 99.69 \text{ minutes}$$

51. For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{10} \log \frac{100}{100-25}$$

$$k = \frac{2.303}{10} \times 0.124 = 0.02$$

$$\therefore t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.02} = 34.65 \text{ min}$$

52. (i) The reaction is of 1st order.

(ii) For first order reaction

$$\ln[R] = -kt + \ln [R]_0$$

comparing eqn. $y = m \times x + c$

we get a straight line with slope = $-k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

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

$$53. t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow k = 60 \text{ s}^{-1}, [R] = \frac{1}{10} [R]_0$$

$$\text{or, } [R]_0 = 10 [R]$$

$$t = \frac{2.303}{60} \log \frac{10[R]}{[R]} \Rightarrow t = \frac{2.303}{60} \log 10$$

$$\Rightarrow t = \frac{2.303 \times 1}{60}$$

$$t = 0.0384 \text{ second}$$

54. The given reaction is



$$\text{At } t = 0 \quad 0.4 \text{ atm} \quad 0 \quad 0$$

$$\text{At time } t \quad (0.4 - x) \text{ atm} \quad x \text{ atm} \quad x \text{ atm}$$

Total pressure at time t will be

$$P_T = (0.4 - x) + x + x = 0.4 + x$$

$$x = (P_T - 0.4)$$

Pressure of SO_2Cl_2 at time t will be

$$p_{\text{SO}_2\text{Cl}_2} = 0.4 - x = 0.4 - (P_T - 0.4) = 0.8 - P_T$$

$$\text{At time } t = 100 \text{ s, } P_T = 0.7 \text{ atm}$$

$$\therefore p_{\text{SO}_2\text{Cl}_2} = 0.8 - 0.7 = 0.1 \text{ atm}$$

According to first order kinetic equation

$$k = \frac{2.303}{t} \log \frac{P_{\text{SO}_2\text{Cl}_2}(\text{initial})}{P_{\text{SO}_2\text{Cl}_2}(\text{after reaction})}$$

$$= \frac{2.303}{100} \log \left(\frac{0.4}{0.1} \right) = 1.3 \times 10^{-2} \text{ s}^{-1}$$

$$55. \text{ (i) } t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$\text{Given } k = 1.06 \times 10^{-3} \text{ min}^{-1}, \frac{[A]_0}{[A]} = \frac{100}{85}$$

$$t = \frac{2.303}{1.06 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{85}$$

$$t = \frac{2303}{1.06} [2 \log 10 - \log 85] \text{ min}$$

$$t = \frac{2303}{1.06} [2 \times 1 - 1.9294] = \frac{2303 \times 0.0706}{1.06}$$

$$t = 153.39 \text{ min} = 153.4 \text{ min.}$$

$$\text{(ii) Given } k = 1.06 \times 10^{-3} \text{ min}^{-1}, \frac{[A]_0}{[A]} = \frac{100}{15}$$

$$t = \frac{2.303}{1.06 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{15}$$

$$= \frac{2303}{1.06} [2 \log 10 - \log 15] \text{ min}$$

$$= \frac{2303}{1.06} [2 \times 1 - 1.1761] = \frac{2303 \times 0.8231}{1.06} \text{ min} = 1788 \text{ min}$$

56. For the first order reaction,

$$\text{Rate constant, } k = \frac{2.303}{100} \log \frac{a}{a-x}$$

For 60% completion of the reaction, if $a = 100\%$

$$a - x = 100 - 60 = 40\%$$

$$\text{Then, } k = \frac{2.303}{100} \log \frac{100}{40} \quad \dots \text{(i)}$$

For 90% completion of the reaction,

$$a = 100\%$$

$$\text{and } a - x = 100 - 90 = 10\%$$

$$\text{Then, } k = \frac{2.303}{t} \log \frac{100}{10} \quad \dots \text{(ii)}$$

Substituting the value of k in eq. (ii),

$$\text{we have, } \frac{2.303}{100} \log \frac{100}{40} = \frac{2.303}{t} \quad [\because \log 10 = 1]$$

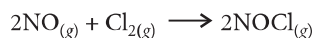
$$\text{or } \frac{1}{t} = \frac{1}{100} \log \frac{100}{40}$$

$$\frac{1}{t} = \frac{0.3979}{100}$$

$$t = \frac{100}{0.3979}$$

$$t = 251 \text{ min}$$

57. Given reaction :



| Exp. No. | Initial [NO] (M) | Initial [Cl ₂] (M) | Initial rate of disapp. of Cl ₂ (M/min) |
|----------|------------------|--------------------------------|--|
| 1. | 0.15 | 0.15 | 0.60 |
| 2. | 0.15 | 0.30 | 1.20 |
| 3. | 0.30 | 0.15 | 2.40 |
| 4. | 0.25 | 0.25 | ? |

(i) Let rate of this reaction $r = k[\text{NO}]^m[\text{Cl}_2]^n$

$$\text{then } \frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$$

$$\text{or } \frac{1}{2} = \left(\frac{1}{2}\right)^n \Rightarrow n = 1$$

$$\text{Again from } \frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^1}{k(0.30)^m(0.15)^1}$$

$$\text{or } \frac{1}{2} = \left(\frac{1}{2}\right)^m \cdot \frac{2}{1} \quad \text{or } \frac{1}{4} = \left(\frac{1}{2}\right)^m \Rightarrow m = 2$$

Hence, expression for rate law is

$$r = k[\text{NO}]^2[\text{Cl}_2]^1$$

(ii) Substituting the values in experiment (1),

$$0.60 \text{ M min}^{-1} = k(0.15 \text{ M})^2 (0.15 \text{ M})^1$$

$$\text{or } k = \frac{0.60 \text{ M min}^{-1}}{0.0225 \times 0.15 \text{ M}^3} = 177.77 \text{ M}^{-2} \text{ min}^{-1}$$

$$\text{(iii) } r = 177.7 \text{ M}^{-2} \text{ min}^{-1} \times (0.25 \text{ M})^2 (0.25 \text{ M}) = 2.77 \text{ M min}^{-1}$$

$$58. \quad k = \frac{2.303}{20 \text{ min}} \log \frac{100}{100-15}$$

$$\frac{2.303}{20 \text{ min}} \log \frac{100}{100-15} = \frac{2.303 \times 0.0706}{20} \text{ min}$$

$$t = \frac{2.303}{k} \log \frac{100}{100-60} = \frac{2.303 \times 20}{2.303 \times 0.0706} \log \frac{100}{40}$$

$$= \frac{20}{0.0706} \times 0.3979 = 112.7 \text{ min}$$

59. (i) When $t = 20 \text{ min}$, $[\text{R}] = 0.289 \text{ mol L}^{-1}$
 $[\text{R}]_0 = 0.400 \text{ mol L}^{-1}$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]}$$

$$\therefore k = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

$$\Rightarrow k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$\Rightarrow k = \frac{2.303}{20} [\log 4.00 - \log 2.89]$$

$$\Rightarrow k = \frac{2.303}{20} [0.6021 - 0.4609]$$

$$\Rightarrow k = \frac{2.303}{20} \times 0.1412$$

$$\Rightarrow k = 2.303 \times 0.00706$$

$$\Rightarrow k = 1.626 \times 10^{-2} \text{ min}^{-1}$$

$$\text{(ii) } t = \frac{2.303}{k} \log \frac{[\text{R}]_0}{[\text{R}]}$$

Here, $[\text{R}]_0 = 0.400 \text{ mol L}^{-1}$, $t = 100 \text{ min}$,
 $k = 1.626 \times 10^{-2} \text{ min}^{-1}$, $[\text{R}] = ?$

$$\therefore 100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{[\text{R}]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[\text{R}]}$$

$$0.7060 = \log \frac{0.4}{[\text{R}]}$$

$$\text{or Antilog } (0.7060) = \frac{0.4}{[\text{R}]}$$

$$5.082 = \frac{0.4}{[\text{R}]} \Rightarrow [\text{R}] = \frac{0.4}{5.082} = 0.079 \text{ M}$$

(iii) Initial rate, *i.e.*, rate of reaction when $t = 0$

When $t = 0.00 \text{ min}$, $[\text{R}] = 0.400 \text{ mol L}^{-1}$

Also, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

$$\therefore \text{Initial rate} = k[\text{R}]$$

$$= 1.626 \times 10^{-2} \text{ min}^{-1} \times 0.400 \text{ mol L}^{-1}$$

$$= 6.504 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

60. (i) Refer answer 59(i).

(ii) Refer answer 59(iii).

$$\text{(iii) } t = \frac{2.303}{k} \log \frac{[\text{R}]_0}{[\text{R}]}$$

Here, $k = 1.6259 \times 10^{-2} \text{ min}^{-1}$, $[\text{R}]_0 = 0.400 \text{ M}$,

$[\text{R}] = 0.350 \text{ M}$

Substituting these values in the equation, we get

$$t = \frac{2.303}{1.6259 \times 10^{-2}} \log \frac{0.400}{0.350}$$

$$= \frac{2.303}{1.6259 \times 10^{-2}} [\log 40 - \log 35]$$

$$= 141.583 [1.6021 - 1.5441] = 141.583 \times 0.0580$$

$$= 8.21 \text{ min}$$

61. Given : $k = 5.10 \times 10^{-3} \text{ min}^{-1}$,

$$t = 3 \times 60 \text{ min} = 180 \text{ min}$$

$$[R]_0 = 0.1 \text{ M}$$

Substituting these values in the equation

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\text{We get, } 180 \text{ min} = \frac{2.303}{5.1 \times 10^{-3} \text{ min}^{-1}} \log \frac{0.1}{[R]}$$

$$\log \frac{0.1}{[R]} = \frac{180 \text{ min} \times 5.1 \times 10^{-3} \text{ min}^{-1}}{2.303} = 0.398$$

$$\frac{0.1}{[R]} = \text{Antilog } 0.398 = 2.50$$

$$[R] = 0.1/2.5 = 0.04 \text{ M}$$

$$62. \text{ (i) } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693$$

$$\text{(ii) } N = N_0 \left(\frac{1}{2}\right)^n$$

$$\text{where, } n = \frac{\text{Total time}}{t_{1/2}} = \frac{60}{10} = 6$$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^6 = \frac{1}{64} \quad \dots(1)$$

[where N_0 = initial amount of reactant and N = amount of reactant left after time, t].

63. 20% decomposition means that $x = 20\%$ of $a = 0.20a$

$$\text{For first order reaction, } k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{15} \log \frac{a}{a-0.20a} = \frac{2.303}{15} \log \frac{a}{0.80a}$$

$$= \frac{2.303}{15} \log 1.25$$

$$= \frac{2.303}{15} \times 0.0969 = 0.0148 \text{ min}^{-1}$$

64. Here $t_{1/2} = 5 \times 10^4 \text{ s}$ and $t = 2 \text{ hours}$
 $= 2 \times 60 \times 60 = 7200 \text{ s}$

$$k = \frac{0.693}{t_{1/2}} \text{ and } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\therefore \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\frac{0.693}{5 \times 10^4} = \frac{2.303}{7200} \log \frac{[A]_0}{[A]}$$

$$\therefore \log \frac{[A]_0}{[A]} = \frac{0.693}{5 \times 10^4} \times \frac{7200}{2.303} = \frac{4989.6}{11.515 \times 10^4}$$

$$= \frac{4989.6}{115150} = 0.0433$$

$$\frac{[A]_0}{[A]} = \text{anti log } 0.0433 = 1.105$$

$$\Rightarrow \frac{[A]}{[A]_0} = \frac{1}{1.105} \times 100 = 90.49\%$$

65. For the first order reaction :

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\text{Let } [A]_0 = x$$

$$\text{then } [A] = x - 20\% \text{ of } x = x - 0.20x = 0.80x$$

$$\therefore k = \frac{2.303}{5} \log \frac{x}{0.80x}$$

$$k = \frac{2.303}{5} \log 1.25 \quad \dots(i)$$

In second case, let $[A]_0 = x$ then

$$[A] = x - 60\% \text{ of } x = x - 0.60x = 0.40x$$

$$\therefore k = \frac{2.303}{t} \log \frac{x}{0.40x}$$

$$k = \frac{2.303}{t} \log 2.5 \quad \dots(ii)$$

From (i) and (ii), we have

$$\frac{2.303}{t} \log 2.5 = \frac{2.303}{5} \log 1.25$$

$$\frac{\log 2.5}{t} = \frac{\log 1.25}{5} \Rightarrow t = \frac{5 \times \log 2.5}{\log 1.25}$$

$$\therefore t = \frac{5 \times 0.3979}{0.0969} = 20.53 \text{ minutes}$$

66. Radioactive decay follows first order kinetics.

$$\text{Let } [A]_0 = 100$$

$$\therefore [A] = 100 \times 80\% = 80$$

$$\text{Decay constant } (k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$$

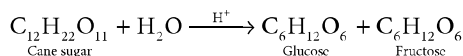
$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} = \frac{2.303}{0.693/5730} \log \frac{100}{80}$$

$$= \frac{2.303 \times 5730}{0.693} \times \log 1.25 = \frac{2.303 \times 5730}{0.693} \times 0.0969$$

$$= \frac{1278.7108}{0.693} = 1845.18 \approx 1845 \text{ years}$$

67. A reaction of second order which obeys the first order rate law is known as pseudo first order reaction.

e.g., Inversion of cane sugar :



$$\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]^1[\text{H}_2\text{O}]^0$$

68. (i) Average rate of reaction between the time interval 30 to 60 seconds is

$$r_{av} = \frac{-[0.17 - 0.31]}{60 - 30} = \frac{0.14}{30} \\ = 4.67 \times 10^{-3} \text{ s}^{-1} \text{ [Taking only difference]}$$

$$(ii) k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

At $t = 30$ s,

$$k = \frac{2.303}{30} \log \frac{0.55}{0.31} = \frac{2.303}{30} \times 0.249 = 1.91 \times 10^{-2} \text{ s}^{-1}$$

At $t = 60$ s,

$$k = \frac{2.303}{60} \log \frac{0.55}{0.17} = \frac{2.303}{90} \times 0.5099 = 1.96 \times 10^{-2} \text{ s}^{-1}$$

At $t = 90$ s

$$k = \frac{2.303}{90} \log \frac{0.55}{0.085}$$

$$k = \frac{2.303}{90} \times 0.8109 = 2.07 \times 10^{-2} \text{ s}^{-1}$$

∴ Average value of k

$$= \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2} + 2.07 \times 10^{-2}}{3} = 1.98 \times 10^{-2} \text{ s}^{-1}$$

69. (i) For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

When $t = 30$ s

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30} = \frac{2.303}{30} \times 0.3010 = 0.0231 \text{ s}^{-1}$$

When $t = 60$ s

$$k = \frac{2.303}{60} \log \frac{0.60}{0.15} = \frac{2.303}{60} \times 0.602 = 0.0231 \text{ s}^{-1}$$

As the value of k is constant at different time intervals, the reaction is first order w.r.t. ester when $[\text{H}_2\text{O}]$ is constant. Hence, it is pseudo first order reaction.

$$(ii) \text{ Average rate} = -\frac{C_2 - C_1}{t_2 - t_1} = \frac{-(0.15 - 0.30)}{60 - 30} \\ = \frac{0.15}{30} = 5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

70. The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by E_a .

$$E_a = E_T - E_R$$

71. The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

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

where $k \rightarrow$ Rate constant

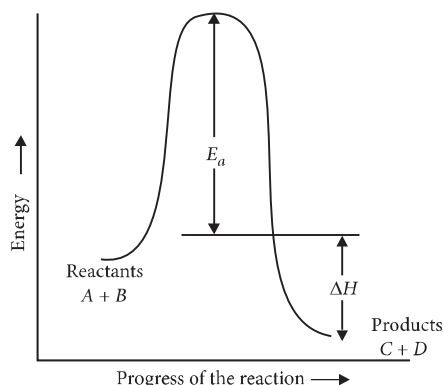
$A \rightarrow$ Arrhenius factor

$R \rightarrow$ Gas constant

$T \rightarrow$ Temperature

$E_a \rightarrow$ Energy of activation for the reaction.

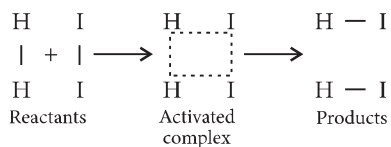
72. The energy required to form activated complex is called activation energy. It is the difference between the threshold energy and the average energy possessed by the reacting molecules.



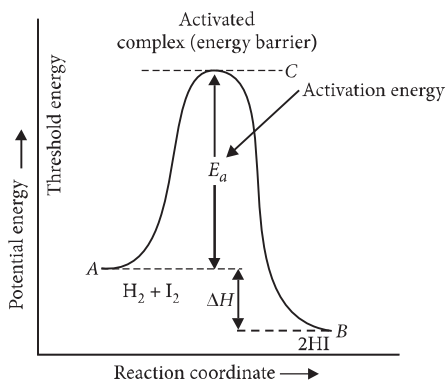
Activation energy (E_a) = Threshold energy – Average energy possessed by reacting molecules.

73. When the colliding molecules possess the kinetic energy equal to E_a , the atomic configuration of species formed at this stage is different from the reactant as well as the products. This stage is called the activated state and the specific configuration bearing state is called activated complex.

For example, in the reaction between $\text{H}_{2(g)}$ and $\text{I}_{2(g)}$, activated complex has configuration in which H—H and I—I bonds are breaking and H—I bonds, are forming as shown below.



Potential energy diagram of this reaction is shown below :



74. Here $k_2 = 2k_1$, $T_1 = 298$ K, $T_2 = 308$ K
 $E_a = ?$

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

$$\log \frac{2k_1}{k_1} = \frac{E_a}{2.303R} \left[\frac{308 - 298}{308 \times 298} \right]$$

$$\log 2 = \frac{E_a}{2.303R} \left[\frac{10}{91784} \right]$$

$$0.3010 = \frac{1.089 \times 10^{-4} E_a}{2.303 \times 8.314}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314}{1.089 \times 10^{-4}} = 52922.77 \text{ J mol}^{-1}$$

75. (i) Order of a reaction : Refer to answer 10.

(ii) Activation energy of a reaction : Refer to answer 70.

76. For first order reaction, $t_{1/2} = \frac{0.693}{k}$

$$t_{1/2} = 200 \text{ min} = 200 \times 60 = 12000 \text{ s}$$

$$\Rightarrow k = \frac{0.693}{12000 \text{ s}} = 5.8 \times 10^{-5} \text{ s}^{-1}$$

Also, for first order decomposition of H_2O_2 , rate constant is

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{ K}$$

Comparing the above equation with the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\Rightarrow E_a = 2.303 \times 8.314 \times 1.0 \times 10^4 = 1.91 \times 10^5 \text{ J mol}^{-1}$$

77. Given, $T_1 = 300$ K, $T_2 = 310$ K

$$k_1 = 2 \times 10^{-2}, k_2 = 4 \times 10^{-2}, E_a = ?$$

Using Arrhenius equation,

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

$$\text{or } \log \frac{4 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{310} \right]$$

$$\text{or } \log 2 = \frac{E_a}{2.303 \times 8.314} \times \left[\frac{310 - 300}{310 \times 300} \right]$$

$$\text{or } E_a = \frac{0.301 \times 2.303 \times 8.314 \times 310 \times 300}{10} = 53598 \text{ J mol}^{-1} = 53.598 \text{ kJ mol}^{-1}$$

78. $k_1 = 0.02 \text{ s}^{-1}$, $k_2 = 0.07 \text{ s}^{-1}$

$$T_1 = 500 \text{ K}, T_2 = 700 \text{ K}$$

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

$$\log \frac{0.07}{0.02} = \frac{E_a}{2.303R} \left[\frac{700 - 500}{700 \times 500} \right]$$

$$E_a = \frac{0.544 \times 2.303 \times 8.314 \times 700 \times 500}{200} = 18228.07 \text{ J mol}^{-1}$$

$$79. \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$E_a = \left(\frac{2.303 \times R \times T_1 \times T_2}{T_2 - T_1} \right) \log \frac{k_2}{k_1}$$

$$E_a = \frac{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 650 \text{ K} \times 700 \text{ K}}{700 \text{ K} - 650 \text{ K}}$$

$$E_a = \frac{19.147 \times 650 \times 700}{50} (\log 23.9 - \log 2.15) \text{ J mol}^{-1}$$

$$= 174237.7 (1.3783 - 0.3324) \text{ J mol}^{-1}$$

$$= 174237.7 \times 1.0459 \text{ J mol}^{-1}$$

$$= 1822235.2 \text{ J mol}^{-1} = 182.24 \text{ kJ mol}^{-1}$$

80. Given : Slope, $m = -4250$ K,

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_a = ?$$

Using formula,

$$\log k = \log A - \frac{E_a}{2.303 R} \left(\frac{1}{T} \right)$$

Comparing with $y = mx + c$ [straight line equation]

$$-\frac{E_a}{2.303 R} = \frac{-4250}{1}$$

$$E_a = 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 4250 \text{ K}$$

$$= 81,375.35 \text{ J mol}^{-1} = 81.37 \text{ kJ mol}^{-1}$$

81. Since the rate of a reaction quadruples when temperature changes from 293 K to 313 K.

$$\therefore k_2 = 4k_1$$

$$T_1 = 293 \text{ K and } T_2 = 313 \text{ K}$$

According to Arrhenius equation

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

Putting the values

$$\log \frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{(313 - 293) \text{ K}}{293 \text{ K} \times 313 \text{ K}} \right]$$

$$0.6021 = \frac{E_a \times 20}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 293 \text{ K} \times 313 \text{ K}}$$

$$\therefore E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20} \text{ J mol}^{-1}$$

$$= 52863.3 \text{ J mol}^{-1} = 52.86 \text{ kJ mol}^{-1}$$

82. $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$, $T_1 = 10 + 273 \text{ K}$, $k_2 = 1.5 \times 10^4 \text{ s}^{-1}$
 $T_2 = ?$ $E_a = 60 \text{ kJ mol}^{-1}$

From Arrhenius equation,

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

$$\text{or } \log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{T_2 - 283}{283 T_2} \right]$$

$$\text{or } \log 3.333 = 3133.63 \left[\frac{T_2 - 283}{283 T_2} \right]$$

$$\text{or } \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283 T_2}$$

$$\text{or } 0.0472 T_2 = T_2 - 283 \text{ or } 0.9528 T_2 = 283$$

$$\text{or } T_2 = \frac{283}{0.9528} = 297 \text{ K or } (297 - 273)^\circ \text{C} = 24^\circ \text{C}$$

83. $T_1 = 295 \text{ K}$, $k_1 = k$ (say)

$$T_2 = 305 \text{ K}, k_2 = 2k, E_a = ?$$

Using Arrhenius equation,

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

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \times \frac{305 - 295}{295 \times 305}$$

$$E_a = \frac{2.303 \times 8.314 \times 295 \times 305 \times \log 2}{10}$$

$$= \frac{2.303 \times 8.314 \times 295 \times 305 \times 0.3010}{10}$$

$$= 51855.2 \text{ J mol}^{-1}$$

84. $k_1 = 6.0 \times 10^{-4} \text{ s}^{-1}$, $T_1 = 300 \text{ K}$, $E_a = 3.05 \times 10^5 \text{ J mol}^{-1}$
 $k_2 = ?$, $T_2 = 310 \text{ K}$

Using Arrhenius equation,

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

$$\text{or, } \log \frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left[\frac{310 - 300}{300 \times 310} \right]$$

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1} \times 10 \text{ K}}{1780684.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\log \frac{k_2}{k_1} = 1.71 \Rightarrow \frac{k_2}{k_1} = \text{antilog}(1.71)$$

$$\frac{k_2}{6 \times 10^{-4}} = 51.28$$

$$k_2 = 3.07 \times 10^{-2} \text{ s}^{-1}$$

85. Here $T_1 = 600 \text{ K}$, $T_2 = 700 \text{ K}$

$$E_a = 209 \text{ kJ/mol} = 209000 \text{ J mol}^{-1}$$

$$k_1 = 1.6 \times 10^{-5} \text{ s}^{-1}$$

Using formula,

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

$$\log k_2 - \log k_1 = \frac{209000}{2.303 \times 8.314} \left[\frac{700 - 600}{700 \times 600} \right]$$

$$\log k_2 - \log (1.60 \times 10^{-5}) = 2.598$$

$$\log k_2 = 2.598 + \log (1.6 \times 10^{-5})$$

$$\log k_2 = -4.796 + 2.598 = -2.198$$

$$k_2 = \text{Antilog}(-2.198)$$

$$\text{or, } k_2 = 6.34 \times 10^{-3} \text{ s}^{-1}$$

86. (i) Refer to answer 72.

(ii) Refer to answer 83.

87. It is due to improper orientation. Energy more than threshold energy and proper orientation are the two main factors which are responsible for a reaction to occur.

