DAY FOURTEEN

Chemical Kinetics

Learning & Revision for the Day

- Rate of a Reaction
- Rate Law and Rate Constant
- Order of Reaction
- Molecularity
- Differential and Integral forms of Different Order Reactions
- Effect of Temperature on Rate of Reaction
- Collision Theory

Chemical kinetics is the branch of chemistry which addresses the rate of chemical reaction. It includes the investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction mechanism and transition rates.

Rate of a Reaction

The rate or speed or velocity of a reaction is the rate of change of concentration of reactants or products in unit time.

$$A \rightarrow B$$

Rate of reaction can be defined in two ways

1. Average rate of reaction, $r_{av} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

   The units of rate of a reaction are mol L^{-1} s^{-1} or mol L^{-1} min^{-1}.
2. Instantaneous rate of reaction (r_{inst}) can be calculated from r_{av} in the limit $\Delta t \rightarrow 0$ and is represented as $r_{inst} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$

   In general for a reaction, $aA + bB \longrightarrow cC + dD$

   $$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Factors Affecting the Rate of Reaction

The rate of chemical reaction depends upon a number of factors such as

(i) concentration
(ii) nature of reactants
(iii) temperature
(iv) presence of catalyst
(v) exposure to radiations

Rate Law and Rate Constant

According to law of mass action, "the rate of a chemical reaction is directly proportional to the product of effective concentrations of reacting species, each raised to a suitable power which may or may not be equal to the respective stoichiometric coefficients."

For a general reaction,

$$aA + bB \longrightarrow \text{Products}; \ \text{Rate} = k[A]^a[B]^b$$

where, k is rate constant or velocity constant or specific reaction rate. The above expression is called **rate law**.

- Rate law cannot be deduced from balanced equation. It is obtained experimentally.
- **Rate constant of reaction** (k) is defined as the rate of reaction when the concentration of each reactant is taken as unity.
- Unit of k in terms of concentration,

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

$$\frac{\text{mol}}{\text{L} \cdot \text{time}} = k\left[\frac{\text{mol}}{\text{L}}\right]^n$$

$$\therefore \quad \text{Unit of } k = (\text{mol})^{1-n} \cdot \text{L}^{n-1}\,\text{s}^{-1}$$

where, n = order of reaction

Order of Reaction

The sum of the powers of the reacting species that are involved in the rate law expression for the reaction represents the **order of the reaction**.

For the reaction, $aA + bB \longrightarrow cC + dD$

According to law of mass action, $\frac{dx}{dt} = k[A]^a[B]^b$

According to rate law (rate equation), $\frac{dx}{dt} = k[A]^\alpha[B]^\beta$

Overall order of reaction $= \alpha + \beta$

The order of reaction can only be determined by experiments.

Molecularity

- Molecularity is defined as the number of ions or molecules or atoms taking part in an elementary process of the reaction mechanism.
- In case of simple reactions, known as elementary reactions, the molecularity is simply the sum of molecules of different reactants as represented by balanced equation, e.g.
  - (i) **Unimolecular reaction** $N_2O_4(g) \longrightarrow 2NO_2(g)$
  - (ii) **Bimolecular reaction** $2HI(g) \longrightarrow H_2(g) + I_2(g)$
  - (iii) **Trimolecular reaction**

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

- In case of complex reactions, i.e. the reactions involving more than one step the rate determining step is the slowest step. The atoms, molecules or ions participating in this step decide the molecularity, e.g.

$$HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2$$

This reaction takes place through following steps:

$$HBrO_3 + HI \xrightarrow[\text{(Rate determining step)}]{\text{Slow}} HBrO_2 + HIO$$

$$HBrO_2 + 4HI \xrightarrow{\text{Fast}} HBr + 2H_2O + 2I_2$$

$$HIO + HI \xrightarrow{\text{Fast}} H_2O + I_2$$

Hence, two molecules participate in slowest step, the reaction is bimolecular type.

NOTE
- **Order of reaction** may change with the condition such as pressure, temperature etc., whereas molecularity does not change.
- **Molecularity** is always a whole number. It can never be zero, negative or fraction whereas, order of a reaction may be whole number, fractional, zero or even negative.

Differential and Integral forms of Different Order Reactions

Zero Order Reaction

Reactions in which the concentration of reactants do not change with time and the concentration, rates remain constant throughout, are said to be zero order reactions.

$$R \longrightarrow P$$

$$\text{Rate} = \frac{-d[R]}{dt} = k[R]^0$$

The integrated rate equation is given as:

$$k = -\frac{[C]_t - [C]_0}{t}$$

where, C_0 = initial concentration of the reactant

C_t = concentration of the reactant at any time t

- Half-life of a reaction is the time required to reduce the concentration of the reactant to half of its initial value.
- Half-life for zero order is given as:

$$t_{1/2} = \frac{[C]_0}{2k}$$

where, k = rate constant, $t_{1/2}$ = half-life period

- For a zero order reaction, half-life period is directly proportional to the initial concentration of reactant and units of rate constant and rate of reaction are same, i.e. mol L^{-1} s^{-1}.

First Order Reaction

The first order reaction is defined as "the reaction in which the rate is determined by the change of one concentration term of the reactant only".

For first order reaction,

$$R \longrightarrow P$$

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

Integrated rate equation is given as:

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

where, t = time, a = initial concentration
k = rate constant,
$(a–x)$ = concentration of a after time 't'

- Half-life of first order reaction is given as:

$$t_{1/2} = \frac{0.693}{k}, \quad t_{1/2} = \text{half-life period}$$

- The unit of rate constant for first order reaction is s^{-1}.
- For any reaction, half-life period, $t_{1/2} \propto \frac{1}{a^{n-1}}$

  where, a = initial concentration, n = order of reaction
- Rate equation for first order gas phase reactions

$$k = \frac{2.303}{t} \log \frac{p_0}{p_0 - p_t}$$

where, p_0 = initial pressure, p_t = pressure after time t

- In a sequence of reactions, $A \xrightarrow{k_A} B \xrightarrow{k_B} C$. $[B]$ is maximum when,

$$t = \frac{2.303}{(k_B - k_A)} \log_{10} \left(\frac{k_B}{k_A}\right)$$

Second Order Reaction

The reaction is said to be of **second order** if its reaction rate is determined by the variation of two concentration terms of reactants.

Its rate equation can be represented as $k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$, when both the reactants are same.

The unit of rate constant for second order reaction is $mol^{-1}\ L\ s^{-1}$.

- Reactions of third and higher orders are rare. This is due to the fact that the chances of three molecules of coming to a single point simultaneously, i.e. probability of trimolecular collisions is much less as compared to unimolecular or bimolecular collisions.
- Sometimes the rate of reaction decreases as the concentration of one of the constituent is increased, such reactions are known as **negative order reactions**. e.g. transformation of ozone into oxygen, i.e.

$$2O_3 \longrightarrow 3O_2$$

$$\text{rate} = -\frac{1}{2}\frac{d}{dt}[O_3] = k\frac{[O_3]^2}{[O_2]} = k[O_3]^2[O_2]^{-1}$$

- When one of the reactants is present in large excess, the second order reaction confirms to the first order and is called **pseudo unimolecular reaction**, e.g. hydrolysis of ester in acidic medium.

$$CH_3COOC_2H_5 \xrightarrow{H^+/H_2O} CH_3COOH + C_2H_5OH$$

  This is also known as pseudo first order reaction.
  Rate $= k[CH_3COOC_2H_5]$

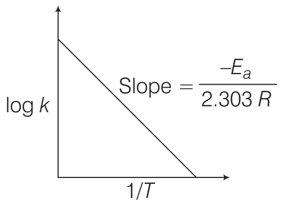
Effect of Temperature on Rate of Reaction

- It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.
- The effect of temperature is usually expressed in terms of temperature coefficient.
- The value of temperature coefficient for most of the reactions lies between 2 to 3.

Arrhenius Theory

The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius equation**.

$$k = Ae^{-E_a/RT} \qquad \text{...(i)}$$



A plot between log K and $1/T$

Here, k = rate constant
A = Arrhenius constant or frequency factor
E_a = activation energy

- It explains that the products are formed through the intermediates or activated complex.
- **Arrhenius equation** is based on two theories of reaction rates, collision theory and transition state theory.

  Since, $k = Ae^{-E_a/RT}$ and E_a is always positive, thus, k always increases with temperature.

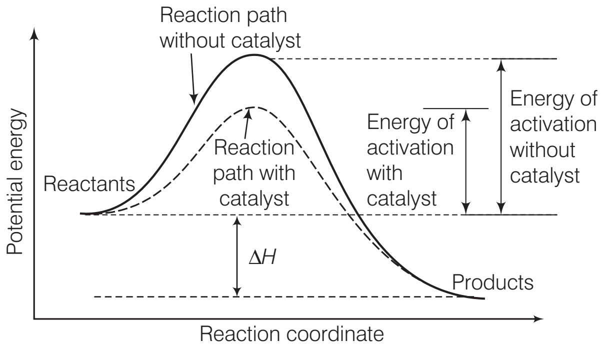
  Due to this rate always increases with temperature whether the reaction is exothermic or endothermic.
- When, $T \longrightarrow \infty$, $k = Ae^0$ or rate constant becomes equal to Arrhenius or frequency factor. (For free radical reaction $E_a = 0$, thus $k = A$ and k becomes independent of temperature).

Activation Energy

- The minimum amount of energy required for a chemical reaction to occur is called **activation energy**. It is represented by E_a.

- Activation energy does not depend on temperature, volume, pressure etc., but gets affected by the presence of catalyst.
- Catalyst increases the rate of reaction by providing alternative path of lower activation energy to the reactants.

  $A \longrightarrow B \; \Delta H < 0$, i.e. exothermic reaction
- Enzyme catalysed reaction are faster than the metal catalysed reaction because they have lower activation energy. Threshold energy is independent of temperature, but E_a shows temperature dependence.



Effect of catalyst on activation energy

Calculation of Activation Energy

Activation energy can be calculated by knowing the rate constants at two different temperatures, assuming that E_a and A remains constant.

Taking log of both the sides in Arrhenius equation, we get

$$\ln k = \ln A - \frac{E_a}{RT}$$

Now, if the values of rate constant at temperatures T_1 and T_2 are k_1 and k_2 respectively then

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad \ldots\text{(i)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \qquad \ldots\text{(ii)}$$

Subtracting the Eq. (i) from (ii), we get

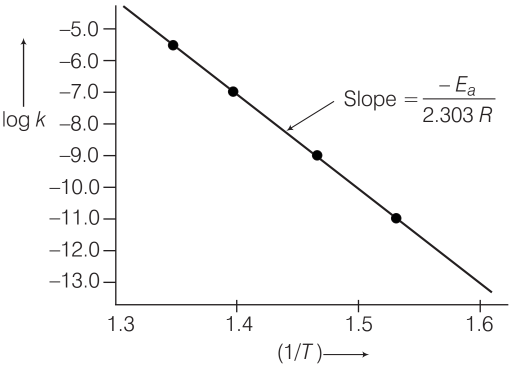
$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right) = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad [\text{Here, } T_2 > T_1]$$

- This relation is used when rate constants at two different temperatures are given.
- This reaction is also written as $\frac{d \log k}{dT} = \frac{E}{RT^2}$
- When $\log k$ is plotted against $1/T$, we get a straight line which is represented by Arrhenius equation as

  $$\log k = \log A - \frac{E_a}{2.303\, RT}$$
- The intercept of this line is equal to log A and slope is equal to $-\frac{E_a}{2.303\, R}$. Therefore, $E_a = -2.303\, R \times \text{slope}$



Plot of log *k vs* 1/*T*

Collision Theory

According to **collision theory**, the reactant molecule are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

- The collisions among the reacting species which results in the products are known as the effective collisions.
- The species taking part in the chemical reaction must have a certain minimum energy known as threshold energy ($E°$).
- Threshold energy = activation energy (E_a) + average energy of molecules.
- If we assume that the rate of reaction is equal to rate of collisions per unit volume or per unit time multiplied by fraction of collisions then the rate constant is given by the expression.

  $$k = Z_{AB}\, e^{-E_a/RT}$$

  where, Z_{AB} = collision frequency factor of reactants A and B
- When steric factor is considered the rate of reaction is given as:

  $$\text{Rate} = PZ_{AB}\, e^{-E_a/RT}$$

  where, P is probability or steric factor.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 A drop of a solution (volume = 0.05 mL) contains 6×10^{-7} mole of H^+.If the rate of disappearance of H^+ is 6.0×10^{5} mol $L^{-1}s^{-1}$, how long will it take for the H^+ in the drop to disappear?

(a) 8.0×10^{-8} s
(b) 2.0×10^{-8} s
(c) 6.0×10^{-6} s
(d) 2.0×10^{-2} s

2 The instantaneous rate of disappearance of MnO_4^- ion in the following reaction is 4.56×10^{-3} M s^{-1}

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

The rate of appearance I_2 is ➞JEE Main (Online) 2013

(a) 4.56×10^{-4} M s^{-1}
(b) 1.14×10^{-2} M s^{-1}
(c) 1.14×10^{-3} M s^{-1}
(d) 5.7×10^{-3} M s^{-1}

3 The rate law for the reaction,

RCl + NaOH(aq) $\longrightarrow$ ROH + NaCl is given by, rate = k [RCl]. The rate of the reaction will be

(a) doubled on doubling the concentration of sodium hydroxide
(b) halved on reducing the concentration of alkyl halide to one half
(c) decreased on increasing the temperature of the reaction
(d) unaffected by increasing the temperature of the reaction

4 The units of second order rate constant is

(a) mol $dm^{-3}s^{-1}$
(b) s^{-1}
(c) $dm^3\, mol^{-1}s^{-1}$
(d) None of these

5 For the reaction system,

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

volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO; the rate of reaction will

(a) diminish to one fourth of its initial value
(b) diminish to one eighth of its initial value
(c) increase to eight times of its initial value
(d) increase to four times of its initial value

6 For the non-stoichiometric reaction, $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

	Initial concentration (A)	Initial concentration (B)	Initial rate of formation of (C) (mol $L^{-1}s^{-1}$)
I	0.1 M	0.1 M	1.2×10^{-3}
II	0.1 M	0.2 M	1.2×10^{-3}
III	0.2 M	0.1 M	2.4×10^{-9}

The rate law for the formation of C is ➞JEE Main 2014

(a) $\frac{dC}{dt} = k[A][B]$
(b) $\frac{dC}{dt} = k[A]^2[B]$
(c) $\frac{dC}{dt} = k[A][B]^2$
(d) $\frac{dC}{dt} = k[A]$

7 Consider a reaction, $aG + bH \longrightarrow$ products,when concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

(a) 0
(b) 1
(c) 2
(d) 3

8 At 518°C, the rate of decomposition of a sample of gases acetaldehyde, initially at a pressure of 363 torr, was 1.00 torr s^{-1} when 5% had reacted and 0.5 torr s^{-1}, when 33% had reacted. The order of the reaction is

(a) 2
(b) 3
(c) 1
(d) 0

9 The rate constant for a zero order reaction is

(a) $k = \frac{C_0}{2t}$
(b) $k = \frac{C_0 - C_t}{t}$
(c) $k = \ln\frac{C_0 - C_t}{t}$
(d) $k = \frac{C_0}{C_t}$

10 The rate for the decomposition of NH_3 on platinum surface is zero order. What are the rate of production of N_2 and H_2 respectively, if $k = 2.5\times10^{-4}$ mol $L^{-1}s^{-1}$?

(a) 1.25×10^{-4} mol L^{-1} s^{-1}; 3.75×10^{-4}mol $L^{-1}s^{-1}$
(b) 3.75×10^{-4} mol L^{-1} s^{-1}; 1.25×10^{-4}mol $L^{-1}s^{-1}$
(c) 2.5×10^{-4} mol L^{-1} s^{-1}; 3.75×10^{-4}mol $L^{-1}s^{-1}$
(d) 1.25×10^{-4} mol L^{-1} s^{-1}; 2.5×10^{-4}mol $L^{-1}s^{-1}$

11 The rate constant of a zero order reaction is 2.0×10^{-2} mol L^{-1} s^{-1}. If the concentration of the reactant after 25 s is 0.5 M, what is the initial concentration?

➞JEE Main (Online) 2013

(a) 0.5 M
(b) 1.25 M
(c) 12.5 M
(d) 1.0 M

12 The time for half-life period of a certain reaction, $A \rightarrow$ products is 1 h. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1}, if it is a zero order reaction? ➞AIEEE 2010

(a) 4 h
(b) 0.5 h
(c) 0.25 h
(d) 1 h

13 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 half of the reaction
(c) 10 times that required for one fourth of the reaction
(d) 20 times that required for half of the reaction

14 A first order reaction is half-completed in 45 min. How long does it need for 99.9% of the reaction to be completed?

(a) 20 h (b) 10 h

(c) $7\frac{1}{2}$ h (d) 5 h

15 For a first order reaction, $A \longrightarrow$ Products, the concentration of A changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of A is 0.01 M is ➞ AIEEE 2012

(a) 1.73×10^{-5} M/min
(b) 3.47×10^{-4} M/min
(c) 3.47×10^{-5} M/min
(d) 1.73×10^{-4} M/min

16 Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. 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 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 $\text{mol}^{-1}\text{dm}^{3}$

17 The half-life period of a first order chemical reaction is 6.93 min. The time required for the completion of 99% of the chemical reaction will be ($\log 2 = 0.301$)

(a) 230.3 min (b) 23.03 min
(c) 46.06 min (d) 460.6 min

18 An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively.

What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? ($\log_{10} 2 = 0.3$) ➞ AIEEE 2012

(a) 2 (b) 3
(c) 6 (d) 9

19 Half-life of a hypothetical reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is

(a) 4 (b) 3
(c) 5 (d) 2

20 The half-life of a second order reaction, $A \longrightarrow B$ is given as

(a) $t_{1/2} = \frac{0.693}{k}$ (b) $t_{1/2} = \frac{k}{[A]_0}$

(c) $t_{1/2} = [A]_0/k$ (d) $t_{1/2} = 1/k[A]_0$

21 The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$
$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is

(a) 1 (b) 0
(c) 3 (d) 2

22 The hydrolysis of methyl formate in acid solution has rate expression : rate $= k\,[HCOOCH_3][H^+]$

The balanced equation being

$$HCOOCH_3 + H_2O \longrightarrow HCOOH + CH_3OH$$

The rate law contains $[H^+]$, though the balanced equation does not contain $[H^+]$ because

(a) H^+ ion is a catalyst
(b) H^+ is an important constituent of any reaction
(c) more for convenience to express the rate law
(d) all acids contain H^+ ions

23 Higher order (> 3) reactions are rare due to ➞ JEE Main 2015

(a) low probability of simultaneous 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 coillisions
(d) loss of active species on collision

24 The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about ➞ AIEEE 2011

(a) 10 times
(b) 24 times
(c) 32 times
(d) 64 times

25 The rate of reaction is doubled for every 10°C rise in temperature. The increase in the reaction rate as a result of temperature rise from 10°C to 100°C is

(a) equal to the energy of activation of products
(b) 112 times
(c) 512 times
(d) 614 times

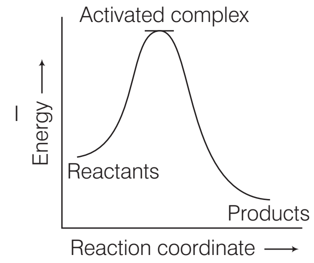
26 The role of a catalyst is to change ....

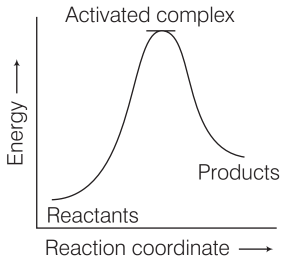
(a) Gibbs energy of reaction
(b) enthalpy of reaction
(c) activation energy of reaction
(d) equilibrium constant

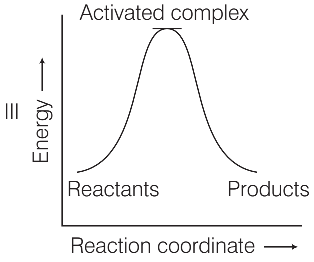
27 For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be

(a) less than ΔH
(b) zero
(c) more than ΔH
(d) equal to ΔH

28 Which of the following graph represents exothermic reaction?







(a) Only (I) (b) Only (II)
(c) Only (III) (d) Both (I) and (II)

29 The reaction, $X \longrightarrow Y$ is an exothermic reaction. Activation energy of the reaction for conversion of X into Y is 150 kJ mol^{-1}. Enthalpy is 135 kJ mol^{-1}. The activation energy for the reverse reaction, $Y \longrightarrow X$ will be

➞ JEE Main (Online) 2013

(a) 280 kJ mol^{-1} (b) 285 kJ mol^{-1}
(c) 270 kJ mol^{-1} (d) 15 kJ mol^{-1}

30 H_2O and O-atom react in upper atmosphere bimolecularly to form two OH radicals. ΔH for the reaction is 72 kJ mol^{-1} at 500 K and energy of activation is 77 kJ mol^{-1}. E_a for bimolecular recombination of two OH radicals to form H_2O and O-atom will be

(a) 5 kJ mol^{-1} (b) 72 kJ mol^{-1}
(c) 77 kJ mol^{-1} (d) 149 kJ mol^{-1}

31 The plot of log k *versus* $\frac{1}{T}$ is linear with a slope of

(a) $-E_a / R$ (b) E_a/R
(c) $-E_a/2.303\,R$ (d) $E_a/2.303\,R$

32 The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be

[$R = 8.314$ JK^{-1} mol^{-1}, log 2 = 0.301] ➞ JEE Main 2013

(a) 48.6 kJ mol^{-1} (b) 58.5 kJ mol^{-1}
(c) 60.5 kJ mol^{-1} (d) 53.6 kJ mol^{-1}

33 A reactant (A) forms two products

$A \xrightarrow{k_1} B$, Activation energy E_{a_1}

$A \xrightarrow{k_2} B$, Activiation energy E_{a_2}

If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 are related as ➞ AIEEE 2011

(a) $k_1 = 2k_2 e^{E_{a_2}/RT}$ (b) $k_1 = k_2 e^{E_{a_1}/RT}$
(c) $k_2 = 2k_1 e^{E_{a_2}/RT}$ (d) $k_1 = Ak_2 e^{E_{a_1}/RT}$

Direction (Q. Nos. 34 and 35) *In the following questions, Assertion* (A) *followed by a Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Both A and R are true and R is correct explanation of A
(b) Both A and R are true but R is not correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

34. **Assertion** (A) Order and molecularity are not same.

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

35. **Assertion** (A) All collisions of reactant molecules do not lead to product formation.

Reason (R) Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Direction (Q. Nos. 36 and 37) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*) *and* (*d*) *given below.*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

36. **Statement I** Order of the reaction can be zero or fractional.

Statement II We cannot determine order from balanced chemical equation.

37. **Statement I** Every collision of reactant molecule is not successful.

Statement II Every collision of reactant molecule with proper orientation is successful one.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Consider the reaction,

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

The rate equation for this reaction is,

$$\text{rate} = k\,[Cl_2]\,[H_2S]$$

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

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

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

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

$Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

(a) Only II
(b) Both I and II
(c) Neither I nor II
(d) Only I

2 The gas phase decomposition of dimethyl ether follows first order kinetics

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in constant volume container at 500°C and has a half-life of 14.5 min. Initially, only dimethyl ether is present at a pressure of 0.4 atmosphere. What is the total pressure of the system after 12 min ?

(a) 0.564 atm
(b) 0.1744 atm
(c) 0.693 atm
(d) 0.249 atm

3 The half-life period for first order reaction having activation energy 39.3 kcal mol^{-1} at 300°C and frequency constant $1.11 \times 10^{11} s^{-1}$ will be

(a) 1 h
(b) 1.68 h
(c) 1.28 h
(d) 1.11 h

4 During nuclear explosion, one of the product is ^{90}Sr with half-life of 28.1 yr. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 yrs and 60 yrs if it is not lost metabolically ?

(Nuclear explosions follow first order kinetics).

(a) 0.7814 μg and 0.227 μg
(b) 0.227 μg and 0.7814 μg
(c) 0.9338 μg and 0.3323 μg
(d) 0.500 μg and 0.300 μg

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

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

(a) Rate constant increases exponentially with increasing activation energy and decreasing temperature
(b) Rate constant decreases exponentially with increasing activation energy
(c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature
(d) Rate constant increases exponentially with decreasing activation energy and increasing temperature

6 The half-life for the reaction, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ is 24 h at 30°C. Starting with 10 g of N_2O_5, how many grams of N_2O_5 will remain after a period of 96 h ?

(a) 1.25 g
(b) 0.63 g
(c) 1.77 g
(d) 0.5 g

7 Rate constant k varies with temperature as given by equation

$$\log k\,(\text{min}^{-1}) = 5 - \frac{2000\text{ K}}{T}$$

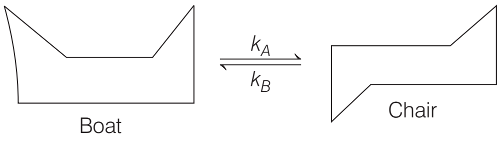
Consider the following about this equation

I. Pre-exponential factor is 10^5
II. E_a is 9.212 kcal
III. Variation of log k with $\frac{1}{T}$ is linear

Select the correct statement.

(a) I, II, III
(b) I, III
(c) II, III
(d) I, II

8 Consider the interconversion of the 'boat' and 'chair conformations of cyclohexane.



The reaction is first order in each direction with an equilibrium constant of 10^4. The activation energy for the conversion of the chair conformer to the boat conformer is 42 kJ mol^{-1}. Assuming an Arrhenius pre-exponential factor of $10^{12}\,s^{-1}$, what is the expected observed reaction rate constant at 298 K if one were to initiate this reaction starting with only the boat conformer?

(a) $8.01 \times 10^5\ s^{-1}$
(b) $4.34 \times 10^8\ s^{-1}$
(c) $2.56 \times 10^7 s^{-1}$
(d) $3.63 \times 10^7\ s^{-1}$

9 For the reaction following data is given

$$A \longrightarrow B; k_1 = 10^{15}\exp\left(\frac{-2000}{T}\right)$$

$$C \longrightarrow D; k_2 = 10^{14}\exp\left(\frac{-1000}{T}\right)$$

At what temperature, k_1 and k_2 will be same?

(a) 434.22 K
(b) 868.43 K
(c) 217.10 K
(d) 130.26 K

10 Select the correct statement.

(a) A collision between reactant molecules must occur with a certain minimum energy before it is effective in yielding product molecule
(b) $\frac{d(\log k)}{dt} = \frac{E_a}{2.303RT^2}$ is called Arrhenius equation
(c) Both (a) and (b)
(d) None of the above

11 Calculate the half-life of the first order reaction,

$$C_2H_4O\,(g) \longrightarrow CH_4\,(g) + CO\,(g)$$

if the initial pressure of C_2H_4O (g) is 80 mm and the total pressure at the end of 20 min is 120 mm.

(a) 40 min (b) 120 min (c) 20 min (d) 80 min

12 The energies of activation for forward and backward reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and backward) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction $(A_2 + B_2 \longrightarrow 2AB)$ in the presence of catalyst will be (in kJ mol^{-1})

(a) 300
(b) –120
(c) 280
(d) – 20

13 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. What will be the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1} ?

(a) 120 kJ mol^{-1}
(b) 80 kJ mol^{-1}
(c) 100 kJ mol^{-1}
(d) 20 kJ mol^{-1}

14 Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 20 kJ mol^{-1}. If k_1 and k_2 are rate constant for reactions R_1 and R_2 respectively at 300 K, then $\ln\left(\frac{k_2}{k_1}\right)$ is equal to $[R = 8.314 \text{J mol}^{-1}\text{ K}^{-1}]$. ➞ JEE Main 2017

(a) 8
(b) 12
(c) 6
(d) 4

15 The chemical reaction, $2O_3 \longrightarrow 3O_2$, proceeds as follows:

$$O_3 \rightleftharpoons O_2 + O \quad \text{(fast)}$$

$$O + O_3 \longrightarrow 2O_2 \quad \text{(slow)}$$

The rate law expression should be

(a) $r = k'[O_3]^2$
(b) $r = k'[O_3]^2[O_2]^{-1}$
(c) $r = k'[O_3][O_2]$
(d) Unpredictable

16 The hydrolysis of sucrose into glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows first order kinetics. In a neutral solution, if at 27°C, rate constant is 2.1×10^{-11} s^{-1} and at 37°C, rate constant is 8.5×10^{-11} s^{-1}. The rate constant at 47°C will be

(a) 4.04
(b) 3.163×10^{-10}
(c) 8.5×10^{-11}
(d) 1.785×10^{-21}

17 Decomposition of H_2O_2 follows a first order reaction. In 50 min, the concentration of H_2O_2 decreases for 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be ➞ JEE Main 2016

(a) 6.93×10^{-4} mol min^{-1}
(b) 2.66 L min^{-1} at STP
(c) 1.34×10^{-2} mol min^{-1}
(d) 6.93×10^{-2} mol min^{-1}

ANSWERS

SESSION 1	**1** (b)	**2** (b)	**3** (b)	**4** (c)	**5** (c)	**6** (d)	**7** (d)	**8** (a)	**9** (b)	**10** (a)
	11 (d)	**12** (c)	**13** (b)	**14** (c)	**15** (b)	**16** (a)	**17** (c)	**18** (d)	**19** (a)	**20** (d)
	21 (d)	**22** (a)	**23** (a)	**24** (c)	**25** (c)	**26** (c)	**27** (c)	**28** (a)	**29** (b)	**30** (a)
	31 (c)	**32** (d)	**33** (b)	**34** (a)	**35** (a)	**36** (b)	**37** (c)			
SESSION 2	**1** (d)	**2** (b)	**3** (b)	**4** (a)	**5** (d)	**6** (b)	**7** (a)	**8** (b)	**9** (a)	**10** (c)
	11 (c)	**12** (d)	**13** (c)	**14** (d)	**15** (b)	**16** (b)	**17** (a)			

Hints and Explanations

SESSION 1

1 $[H^+] = \dfrac{6\times10^{-7}\text{ mol}}{0.05\times10^{-3}\text{L}} = 1.2\times10^{-2}\text{ M}$

$$\text{or } r = \frac{\Delta x}{\Delta t} \text{ or } \Delta t = \frac{\Delta x}{r} = \frac{1.2\times10^{-2}\text{ M}}{6\times10^{5}\text{ Ms}^{-1}}$$

$$\therefore \qquad t = 2\times10^{-8}\text{ s}$$

2 Rate of reaction $= \dfrac{-1}{2}[MnO_4] = \dfrac{1}{5}[I_2]$

$\therefore$ Given, rate of disappearance of

$$MnO_4^- = d\frac{[MnO_4^-]}{dt} = 4.56\times10^{-3}$$

$\because$ Rate of appearance of I_2

$$= \frac{5}{2}\times4.56\times10^{-3}$$

$$= 11.4\times10^{-3} = 1.14\times10^{-2}\text{ Ms}^{-1}$$

3 As rate $= k[RCl]$, on decreasing the concentration of RCl to half, the rate will also be halved.

4 For second order, $\dfrac{dx}{dt} = k(\text{conc.})^2$

$$\text{Hence,} \quad k = \frac{\text{conc.}}{\text{time}}\times\frac{1}{(\text{conc.})^2}$$

$$= (\text{conc.})^{-1}\cdot\text{time}^{-1}$$

$$= \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}$$

5 $\left(\dfrac{dx}{dt}\right) = k[NO]^2[O_2] = k\left(\dfrac{n_{NO}}{V}\right)^2\left(\dfrac{n_{O_2}}{V}\right)$

$$\left(\frac{dx}{dt}\right) = \frac{k}{V^3}(n_{NO})^2(n_{O_2})$$

$$\left(\frac{dx}{dt}\right)' = \frac{k(n_{NO})^2(n_{O_2})}{\left(\frac{V}{2}\right)^3} = 8\left(\frac{dx}{dt}\right)$$

6 $r = \dfrac{dC}{dt} = k[A]^x[B]^y$

$$1.2\times10^{-3} = k(0.1)^x(0.1)^y \qquad \ldots\text{(i)}$$

$$1.2\times10^{-3} = k(0.1)^x(0.2)^y \qquad \ldots\text{(ii)}$$

$$2.4\times10^{-9} = k(0.2)^x(0.1)^y \qquad \ldots\text{(iii)}$$

As shown above, rate of reaction remains constant as the concentration of reactant B changes from 0.1M to 0.2 M and becomes double when concentration of A changes from 0.1 to 0.2 (i.e. doubled).

$$\therefore \qquad r = k[A]^1[B]^0$$

7 $aG + bH \longrightarrow$ products

Let the rate of reaction be

$$r = k[G]^a[H]^b \qquad \ldots\text{(i)}$$

When concentration of both reactants G and H is doubled, rate increases by eight times,

$$\therefore \qquad 8r_1 = k[2G]^a[2H]^b \qquad \ldots\text{(ii)}$$

When concentration of G is doubled, keeping the concentration of H fixed, rate is doubled,

$$\therefore \qquad 2r_2 = k[2G]^a[H]^b \qquad \ldots\text{(iii)}$$

On solving Eq (ii) and (iii), we have

$$b = 2$$

On solving Eq (i) and (iii), we have

$$a = 1$$

$\therefore$ Overall order of the reaction

$$= a + b = 1 + 2 = 3$$

8 For the reaction,

$$CH_3CHO(g) \xrightarrow{\text{Decomposes}} CH_4 + CO$$

Let order of reaction with respect to CH_3CHO is m. Its given, $r_1 = 1$ torr/sec when CH_3CHO is 5% reacted, i.e. 95% unreacted. Similarly, $r_2 = 0.5$ torr/sec when CH_3CHO is 33% reacted, i.e. 67% unreacted.

Use the formula,

$$r \propto (a - x)^m$$

where, $(a - x)$ = amount unreacted

$$\text{so,} \quad \frac{r_1}{r_2} = \frac{(a - x_1)^m}{(a - x_2)^m} \text{ or } \frac{r_1}{r_2} = \left[\frac{a - x_1}{a - x_2}\right]^m$$

Now, putting the given values

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)$$

$$\Rightarrow \qquad 2 = (1.41)^m \text{ or } m = 2$$

Therefore, the order of reaction is 2.

9 For a zero order reaction,

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

$$\int_{C_0}^{C_t} d[A] = k\int_{t=0}^{t=t} dt$$

$$C_0 - C_t = kt \Rightarrow k = \frac{C_0 - C_t}{t}$$

10 $2NH_3 \longrightarrow N_2 + 3H_2$

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

$$\text{Rate} = k[NH_3]^0$$

$$\text{or} \quad \frac{d[NH_3]}{dt} = 2.5\times10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$$

$$\frac{d[N_2]}{dt} = \frac{1}{2}\times2.5\times10^{-4}$$

$$\frac{d[N_2]}{dt} = 1.25\times10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$$

$$\frac{d[H_2]}{dt} = \frac{3}{2}\times2.5\times10^{-4}$$

$$= 3.75\times10^{-4}\text{mol L}^{-1}\text{ s}^{-1}$$

11 For zero order reaction,

$$\text{rate} = \frac{dx}{dt} = k$$

$$= \frac{x_1 - x_2}{dt} = 2.0\times10^{-2}$$

$$\frac{x_1 - 0.5}{25} = 2.0\times10^{-2}$$

(Here, x_1 = initial concentration)

$$x_1 - 0.5 = 0.5 = 0.5 + 0.5 = 1.0\text{ M}$$

12 For a zero order reaction, $k_0 = \dfrac{[A]_0}{2t_{1/2}}$

Since, $[A]_0 = 2$ M, $t_{1/2} = 1$ h

$$\text{So,} \quad k_0 = 1 \text{ and } k_0 = \frac{\Delta x}{t}$$

$$\text{or} \quad t = \frac{0.50 - 0.25}{1} = 0.25\text{ h}$$

13 $k = \dfrac{1}{t}\ln\dfrac{100}{100 - 99.9} = \dfrac{1}{t}\ln\dfrac{100}{0.1}$

$$\text{or} \quad \frac{\ln 2}{t_{1/2}} = \frac{1}{t}\ln 10^3$$

$$\text{or} \quad \frac{\log 2}{t_{1/2}} = \frac{1}{t}\times\log 10^3 = \frac{3}{t}$$

$$t_{1/2} = \frac{\log 2}{3}\times t = \frac{0.30103}{3}\times t \approx 0.10t$$

14 $k = \dfrac{0.693}{45}\text{min}^{-1} = \dfrac{2.303}{t_{99.9\%}}\log\dfrac{a}{a - 0.999a}$

$$[\because a = 1]$$

$$\text{or} \quad t_{99.9\%} = \frac{2.303\times45}{0.693}\log 10^3$$

$$= 448\text{ min} \approx 7\frac{1}{2}\text{h}$$

15 By first order kinetic, rate constant

$$k = \frac{2.303}{t}\log\left(\frac{a}{a - x}\right)$$

$$a = 0.1\text{ M}$$

$$(a - x) = 0.025\text{ M}$$

$$t = 40\text{ min}$$

$$\therefore \quad k = \frac{2.303}{40}\log\frac{0.1\text{M}}{0.025\text{ M}}$$

$$= 0.0347\text{ min}^{-1}$$

$$\text{Rate} = \left(\frac{dx}{dt}\right) = k[A]^1 = 0.0347\times0.01$$

$$= 3.47\times10^{-4}\text{ M min}^{-1}$$

16 First order kinetics,

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}\,s^{-1}$$

Zero order kinetics, $k_0 = \frac{C_0}{2t_{1/2}} = \frac{1.386}{2\times 20}$

Hence, $\frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5$

17 Half-life, $t_{1/2}$= 6.93 min, $k_1 = \frac{0.693}{6.93} = 0.1$

$$k_1 = \frac{2.303}{t}\log\left(\frac{100}{100-99}\right)$$

$$0.1 = \frac{2.303}{t}\times\log\frac{100}{1} = \frac{2.303}{t}\log 10^2$$

$$t = \frac{2.303\times 2}{0.1} = 46.06\text{ min}$$

18 For a first order process, $kt = \ln\frac{[A]_0}{[A]}$

where, $[A]_0$ = initial concentration.

$[A]$ = concentration of reactant remaining at time t.

$$kt_{1/8} = \ln\frac{[A]_0}{[A]_0/8} = \ln 8 \qquad \ldots\text{(i)}$$

$$kt_{1/10} = \ln\frac{[A]_0}{[A]_0/10} = \ln 10 \qquad \ldots\text{(ii)}$$

Therefore, $\frac{t_{1/8}}{t_{1/10}} = \frac{\ln 8}{\ln 10} = \log 8 = 3\log 2$

$$\frac{t_{1/8}}{t_{1/10}} = 3\times 0.3 = 0.9$$

$$\frac{t_{1/8}}{t_{1/10}}\times 10 = 0.9\times 10 = 9.0$$

19 Since, as we know that, $t_{1/2}\propto\frac{1}{a^{n-1}}$

Hence, $t_{1/2}\propto a^{1/3}$, only when $n = 4$

20 For any reaction, halt-life $(t_{1/2})\propto\frac{1}{a^{n-1}}$

For 2nd order $n = 2$

$\therefore\quad t_{1/2}\propto\frac{1}{[A]_0^{2-1}}\Rightarrow t_{1/2} = \frac{1}{k[A]_0}$

21 As 2nd step is rate determining step.

Rate $= k[NOBr_2][NO] \qquad \ldots$(i)

But, $NOBr_2$ is in equilibrium

$$K_{eq} = \frac{[NOBr_2]}{[NO][Br_2]}$$

$[NOBr_2] = K_{eq}[NO][Br_2] \qquad \ldots$(ii)

Putting the $[NOBr_2]$ in Eq (i)

$$\text{Rate} = k\cdot K_{eq}\,[NO][Br_2][NO]$$

Hence, Rate $= k\cdot K_{eq}[NO]^2[Br_2]$

$$\text{Rate} = k'[NO]^2[Br_2] \qquad [k' = k\cdot K_{eq}]$$

Hence, order of reaction with respect to NO is two.

22 H^+ ions act as catalyst for the given reaction.

$$HCOOCH_3 + H_2O \longrightarrow HCOOH + CH_3OH$$

23 The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants.

Since, the chances of simultaneous collision with proper orientation between more than 3 species is very rare, so reaction with order greater than 3 are rare.

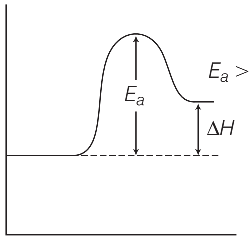
24 For every 10°C rise of temperature, rate is doubled. Thus, temperature coefficient of the reaction = 2.

When temperature is increased by 50°, rate becomes = $2^{\left(\frac{50}{10}\right)} = 2^5$ times = 32 times

25 Increase in steps of 10°C has been made 9 times, hence rate of reaction should increase 2^9 times, i.e. 512 times.

26 A catalyst lowers the activation energy of reaction.

27 The minimum value for the energy of activation will be more than ΔH.



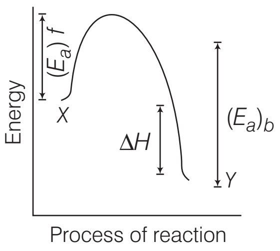
28 Graph (I) only represents exothermic reaction because products have lesser energy than reactants ($\Delta H < 0$).

29 An exothermic reaction can be represented as :

$$X \longrightarrow Y + \text{energy}$$

i.e. energy of $Y << X$

So, the energy profile diagram is



$\therefore\qquad (E_a)_f + \Delta H = (E_a)_b$

$\qquad 150 + 135 = (E_a)_b$

$\qquad (E_a)_b = 285\text{ kJ mol}^{-1}$

30 $H_2O + O \xrightarrow{E_a} 2OH;\ \Delta H = 72\text{ kJmol}^{-1}$

$2OH \xrightarrow{E_b} H_2O + O;\ \Delta H = -\,72\text{ kJmol}^{-1}$

Also $\qquad E_a - E_b = \Delta H$

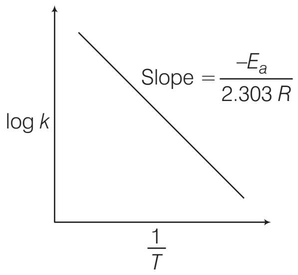
or $\qquad 77 - E_b = 72$

$\therefore\qquad E_b = 5\text{ kJ mol}^{-1}$

31 According to Arrhenius equation,

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

When log k is plotted against $\frac{1}{T}$, we get a straight line, where intercept of this line is equal to log A and slope is $\frac{-E_a}{2.303R}$.



32 As per Arrhenius equation,

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

$$2.303\log 2 = \frac{-E_a}{8.314}\left[\frac{1}{310} - \frac{1}{300}\right]$$

$\Rightarrow\qquad E_a = 53.6\text{ kJ/mol}$

33 $A \xrightarrow{k_1} B,\ A \xrightarrow{k_2} C$

By Arrhenius equation,

$$k_1 = A'e^{-E_{a_1}/RT}$$

and $\quad k_2 = A'e^{-E_{a_2}/RT}$

[A' is Arrhenius constant]

$\because\qquad E_{a_2} = 2E_{a_1}$

$\therefore\qquad k_2 = A'e^{-2E_{a_1}/RT}$

$$\frac{k_1}{k_2} = \frac{A'e^{-E_{a_1}/RT}}{A'e^{-2E_{a_1}/RT}} = e^{E_{a_1}/RT}$$

$\therefore\qquad k_1 = k_2e^{E_{a_1}/RT}$

34 Order may or may not be equal to molecularity. It is determined experimentally and molecularity is the sum of the stoichiometric coefficients of rate determining elementary step.

35 All collisions of reactant molecules do not lead to product formation. Only effective collisions having proper orientation and sufficient kinetic energy lead to compound formation.

36 The order of reaction can only be determined by experiments. Hence, option (b) is correct.

37 A successful collision leads to a chemical reaction, when the reactant molecules collide with proper orientation and attain threshold energy level. Hence, option (c) is correct.

SESSION 2

1 Slowest step is the rate determining step. Thus, in case (*A*), rate law is given as rate = $k[Cl_2][H_2S]$

While for the reaction given in case (*B*), rate law is given as rate $= k[H_2S][Cl_2][H^+]^{-1}$.

Hence, only mechanism (*A*) is consistent with the given rate law.

2

$$\begin{array}{lccccccc} & CH_3OCH_3(g) & \rightarrow & CH_4(g) & + & H_2(g) & + & CO(g) \\ \text{At, } t = 0 & p_0 & & 0 & & 0 & & 0 \\ \text{At. } t & p_0 - p & & p & & p & & p \end{array}$$

Total pressure at $t = p_0 + 2p$

Rate expression for first order kinetics :

$$\log \frac{p_0 - p}{p_0} = -\left(\frac{k}{2.303}\right)t$$

$$= -\left(\frac{0.693/t_{1/2}}{2.303}\right)t$$

$$= -\frac{0.693 / 14.5 \text{ min}}{2.303} \times 12 \text{ min}$$

or $\log \dfrac{p_0 - p}{p_0} = -0.249$

or $\dfrac{p_0 - p}{p_0} = 0.564$

or $p = p_0 - 0.564 p_0$

$= p_0(1 - 0.564)$

$= (0.40 \text{ atm})(0.436)$

$= 0.1744 \text{ atm}$

3 Given, $A = 1.11 \times 10^{11} s^{-1}$;

$E_a = 39.3 \times 10^3$ cal mol^{-1}

$R = 1.987$ cal; $T = 573$ K

$\because \log_{10} k = \log_{10} A - \dfrac{E_a}{2.303RT}$

or $\log_{10} k = \log_{10} 1.11 \times 10^{11} - \left\{\dfrac{39.3 \times 10^3}{2.303 \times 1.987 \times 573}\right\}$

or $k = 1.14 \times 10^{-4}$ s^{-1}

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.14 \times 10^{-4}} = 6078 \text{ s}$$

$= 1.69$ h

4 Since, nuclear explosion follows the first order kinetics

$\because t_{1/2}$ of $^{90}Sr = 28.1$ yr

$\therefore t_{1/2} = \dfrac{0.693}{k}$

$\therefore k = \dfrac{0.693}{28.1}$ yr^{-1}

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

[Here, $a = 1\,\mu g$]

At $t = 10$ yr;

$$10 = \frac{2.303 \times 28.1}{0.693} \log \frac{1}{(a - x)}$$

$\therefore$ Amount of Sr left $= (a - x) = 0.7814\,\mu g$

At $t = 60$ yr;

$$60 = \frac{2.303 \times 28.1}{0.693} \log \frac{1}{(a - x)}$$

$\therefore (a - x) = 0.227\,\mu g$

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

6 $k = \dfrac{0.693}{24} h^{-1} = \dfrac{2.303}{96} \log \dfrac{10}{a - x}$

or $\log \dfrac{10}{a - x} = 1.2036$

or $1 - \log(a - x) = 1.2036$

or $\log(a - x) = -0.2036$

$= +\,1.7964 - 2$

or $(a - x) = \text{antilog}(1.7964 - 2)$

$= 0.6258 = 0.63$ g

7 $\log k \,(\text{min}^{-1}) = 5 - \dfrac{2000 \text{ K}}{T}$

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

I. $\log A = 5$, $A = 10^5$ is true

II. $\dfrac{E_a}{2.303\,R} = 2000$

$E_a = 2000 \times 2.303 \times 0.002$ kcal

$= 9.212$ kcal, true

III. Equation represents straight line, hence, true.

8 $k_B = Ae^{-E_a/RT} = 10^{12}\, e^{-42000/8.314 \times 298}$

$= 4.34 \times 10^4$ s^{-1}

Also, $K_C = 10^4$ and

$$K_C = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}}$$

$$10^4 = \frac{k_A}{k_B}$$

$\therefore k_A = 10^4\, k_B = 4.34 \times 10^8$ s^{-1}

Expected observed reaction rate constant $= k_A + k_B = 4.34 \times 10^8$ s^{-1}

9 $k_1 = k_2$

$$10^{15} e^{\left(\frac{-2000}{T}\right)} = 10^{14} e^{\left(\frac{-1000}{T}\right)}$$

or $15 - \dfrac{2000}{T \times 2.303} = 14 - \dfrac{1000}{T \times 2.303}$

or $\dfrac{1000}{T \times 2.303} = 1$

$\therefore T = 434.22$ K

10 According to Arrhenius equation,

$\ln k = \ln A - E_a/RT$

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

Differentiating both sides, we get

$$\frac{d \log k}{dt} = \frac{E_a}{2.303RT^2}$$

Both statements(a) and (b) are correct.

11

$$\begin{array}{lccccc} & C_2H_4O(g) & \longrightarrow & CH_4(g) & + & CO(g) \\ \text{At } t_0 & p_0 & & 0 & & 0 \\ \text{At } t_{20} & p_0 - p & & p & & p \end{array}$$

Initial pressure, $p_0 = 80$ mm

Total pressure after 20 min,

$p_{\text{total}} = p_0 - p + p + p$

$= p_0 + p$

$120 = 80 + p$

or $p = 120 - 80 = 40$ mm

$$k = \frac{2.303}{20} \log \frac{80}{40} = \frac{2.303}{20} \log 2$$

$[\because \log 2 = 0.3010]$

$$k = \frac{2.303 \times 0.3010}{20} = \frac{0.693}{20}$$

We know that, $t_{1/2} = \dfrac{0.693}{k}$

By putting the value of k in this equation we get,

$$t_{1/2} = \frac{0.693 \times 20}{0.693} = 20 \text{ min}$$

12 $A_2 + B_2 \rightleftharpoons 2AB$

E_a (forward) = 180 kJ mol^{-1}

E_a (backward) = 200 kJ mol^{-1}

In the presence of catalyst,

E_a (forward) = 180 – 100 = 80 kJ mol^{-1}

E_a (backward) = 200 – 100

= 100 kJ mol^{-1}

$\Delta H = E_a$ (forward) – E_a (backward)

= 80 – 100 = – 20 kJ mol^{-1}

13 Let E_a = activation energy in the presence of catalyst

$E_a{}'$ = activation energy in the absence of catalyst

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

In the presence of catalyst :

$$k_1 = Ae^{-E_a/(R\times 500)}$$

In the absence of catalyst :

$$k_2 = Ae^{-E'a/(R\times 400)}$$

Given, the rates are same, i.e. $r_1 = r_2$

$$\therefore \; e^{-E_a/(R\times 500)} = e^{-E_a{}'/(R\times 400)}$$

or $$\frac{E_a}{R\times 500} = \frac{E_a{}'}{R\times 400}$$

or $$\frac{E_a}{500} = \frac{E_a - 20}{400}$$

$[\because E_a - E_a{}' = 20]$

or $$E_a = 100 \text{ kJ mol}^{-1}$$

14 According to Arrhenius equation,

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

where, A = frequency factor or pre-exponential factor.

R = gas constant

T = absolute temperature

E_a = energy of activation

For reaction R_1, $k_1 = Ae^{-E_{a_1}/RT}$ ...(i)

For reaction R_2, $k_2 = Ae^{-E_{a_2}/RT}$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{k_2}{k_1} = e^{-\frac{(E_{a_2} - E_{a_1})}{RT}} \quad \text{...(iii)}$$

[∵ Pre-exponential factor 'A' is same for both reactions]

Taking ln on both sides of Eq. (iii), we get

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a_1} - E_{a_2}}{RT}$$

Given, $E_{a_1} = E_{a_2} + 10 \text{ kJ mol}^{-1}$

$= E_{a_2} + 10{,}000 \text{ J mol}^{-1}$

$$\therefore \quad \ln\frac{k_2}{k_1} = \frac{10{,}000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K}}$$

$= 4$

15 From the step (ii), Rate, $r = k[\text{O}][\text{O}_3]$ ...(i)

For fast reaction, $$K_C = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}$$

or $$[\text{O}] = \frac{K_C[\text{O}_3]}{[\text{O}_2]}$$

On putting the value of [O] in Eq. (i), we get

$$\text{Rate, } r = k\cdot\frac{K_C[\text{O}_3]}{[\text{O}_2]}[\text{O}_3]$$

$$= k\cdot K_C[\text{O}_3]^2[\text{O}_2]^{-1} = k'[\text{O}_3]^2[\text{O}_2]^{-1}$$

where, $k' = k\cdot K_C$

16 $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log\frac{8.5\times 10^{-11}}{2.1\times 10^{-11}} = \frac{E_a}{2.303\times 8.314}\left[\frac{10}{300\times 310}\right]$$

$\therefore \quad E_a = 108.1$ kJ

$$\log k = \log A - \frac{E_a}{2.303RT_1}$$

$$\log 2.1\times 10^{-11} = \log A - \frac{108.1\times 10^3}{2.303\times 8.314\times 300}$$

$\therefore A = 13.87\times 10^7$

$$\log (k)_{47^\circ\text{C}} = \log A - \frac{E_a}{2.303\times R\times T}$$

$$= \log 13.87\times 10^7 - \frac{108.1\times 10^3}{2.303\times 8.314\times 320}$$

$= 3.163\times 10^{-10} \text{ s}^{-1}$

17 For first order reaction,

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

Given, $t = 50$ min, $a = 0.5$ M,
$a - x = 0.125$ M

$$\therefore \quad k = \frac{2.303}{50}\log\frac{0.5}{0.125} = 0.0277 \text{ min}^{-1}$$

Now, as per reaction

$$2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$$

$$-\frac{1}{2}\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{1}{2}\frac{d[\text{H}_2\text{O}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

Rate of reaction, $$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2]$$

$$\therefore \quad \frac{d[\text{O}_2]}{dt} = -\frac{1}{2}\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{1}{2}k[\text{H}_2\text{O}_2] \quad \text{...(i)}$$

When the concentration of H_2O_2 reaches 0.05 M,

$$\frac{d[\text{O}_2]}{dt} = \frac{1}{2}\times 0.0277\times 0.05 \text{ [from Eq.(i)]}$$

or $$\frac{d[\text{O}_2]}{dt} = 6.93\times 10^{-4} \text{ mol min}^{-1}$$

Alternative Method

In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M or in one half-life, concentration of H_2O_2 decreases from 0.5 to 0.25 M. In two half-lives, concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2t_{1/2} = 50$ min, $t_{1/2} = 25$ min

$$\therefore \quad k = \left(\frac{0.693}{25}\right)\text{min}^{-1}$$

or $$\frac{d[\text{O}_2]}{dt} = -\frac{1}{2}\frac{d[\text{H}_2\text{O}_2]}{dt}$$

$$= \frac{k[\text{H}_2\text{O}_2]}{2}$$

$$= 6.93\times 10^{-4} \text{ mol min}^{-1}$$