DAY TWENTY TWO

Chemical Kinetics

Learning & Revision for the Day

- Rate of a Reaction
- Molecularity
- Order of Reaction
- Integrated Rate Equations and Half-life
- Zero Order Reaction
- First Order Reaction
- Arrhenius Equation
- Activation Energy
- Collision Theory

The feasibility of a reaction can be predicted with the help of thermodynamic principle but it does not deal with the rate at which chemical reaction occurs. The branch of chemistry which deals with the study of rate of reactions, factor affecting the rate of reaction and mechanism of the reaction is known as **chemical kinetics**.

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.

$$A \longrightarrow B$$

It can be defined in two ways:

(i) **Average rate of reaction,** can be represented as $r_{\text{av}} = -\dfrac{\Delta[A]}{\Delta t} = +\dfrac{\Delta[B]}{\Delta t}$

The units of rate of a reaction are mol $\text{L}^{-1}\,\text{s}^{-1}$ or mol $\text{L}^{-1}\,\text{min}^{-1}$.

(ii) **Instantaneous rate of reaction** (r_{inst}) can be calculated from r_{av} in the limit $\Delta t \to 0$ and represented as

$$r_{\text{inst}} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

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

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

NOTE The negative sign in the rate of a reaction, indicates that the concentration of reactants decreases (disappearance of reactants) with time, while the positive sign indicates that the concentration of products increases (formation of products) with time.

Factors Affecting the Rate of a Reaction

The factors which affect the rate of reaction are as follows:

(i) **Concentration of reactants** An increase in concentration of reactants, brings more frequent collisions between the reacting molecules. That increases the rate of reaction.

(ii) **Nature of reactants** The nature of bonds in a molecule influences the rate of reaction at which it changes into products.

(iii) **Temperature** Reaction rates are normally favoured by increase of temperature. Increase in temperature causes a greater fraction of the molecules to have an energy at least equal to the threshold energy.

(iv) **Presence of catalyst** Presence of catalyst increases the rate of reaction by lowering the energy barrier.

(v) **Surface area of reactants** The rate of reaction increases as the surface area of the reactants increases.

(vi) **Presence of light** Reaction rate normally becomes faster in presence of light.

Rate Law and Specific 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, may or may not be equal to the respective stoichiometric coefficients.

  For a general reaction,

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

  $$\frac{-d[R]}{dt} = k\,[A]^a\,[B]^b$$

  The above equation is called differential rate equation and k is rate constant or velocity constant or specific reaction rate.

- The above expression is called **rate law** as it describes the functional dependence of the reaction rate upon concentration of various reactants. Rate law cannot be deduced from balanced equation. It is obtained experimentally.

- Unit of k in terms of concentration, Rate $= k[A]^x$

  Unit of concentration $= \dfrac{\text{mol}}{\text{Ls}}$

  $$\therefore \qquad \text{Rate} = k\left(\frac{\text{mol}}{\text{Ls}}\right)^x$$

  $$\therefore \qquad \text{Unit of } k = (\text{mol})^{1-x} \cdot \text{L}^{x-1}\text{s}^{-1}$$

  where, x = order of reaction

Molecularity

- It is defined as the number of ions or molecules or atoms taking part in an elementary process of the reaction mechanism. It is always a whole number and can never be zero, negative or fractional.

- 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 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:

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

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

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

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

Order of Reaction

It is defined as the sum of the coefficients (or powers) of the reacting species that are involved in the rate law expression for the reaction. For the reaction, $aA + bB \longrightarrow cC + dD$

Rate law (rate equation) is given as : $\dfrac{dx}{dt} = k[A]^\alpha[B]^\beta$

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

It can only be determined by experiments. It may be whole number, fraction, zero or negative.

Integrated Rate Equations and Half-life

- The differential rate equation is integrated to get a reaction between directly measured experimental data, i.e. concentrations at different time and rate constant. The obtained equation are known as **integrated rate equation**.

- **Half-life time** period is the time required to reduce the concentration of the reactant to half of its initial value.

  The integrated rate equations and half life period are different for the reactions of different orders. These are given below for zero and first order reactions.

Zero Order Reaction

- In these reactions, in which the concentration of reactants do not change with time and the concentration rates remain constant throughout.

  $$k = -\frac{[C_t] - [C_0]}{t}$$

where, C_0 = initial concentration of the reactant
C_t = concentration of the reactant at any time t

- Half-life period for these reaction is equal to,

$$t_{1/2} = \frac{C_0}{2k},\ t_{1/2} \propto C_0$$

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

- Units of rate constant and rate of reaction are same, i.e. mol L^{-1} s^{-1}.

First Order Reaction

- In these are reactions, the reaction rate is determined by the change of one concentration term of the reactant only,

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

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

- Half-life period of these reactions is,

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

- 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,

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

NOTE For reaction, $2A \longrightarrow B$

Rate = $k\,[A]^2$, i.e. the reaction follows second order rate kinetics and the half-life of second order is equals to,

$$t_{l/2} = \frac{1}{k[A_o]}$$

- Sometimes, the rate of reaction decreases as the concentration of one of the constituent is increased. These reaction are called **negative order reactions**. e.g. transformation of ozone into oxygen,

$$2O_3 \longrightarrow 3O_2$$

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

- 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.

$$\text{Rate} = k\,[\text{Ester}]$$

Comparative Study of Zero and First Order Reactions

Reaction	Order	Rate law equation	Expression for rate constant	Half-life period
$A \longrightarrow$ product	0	Rate = k	$k = \frac{[A_0]-[A]}{t}$	$t_{1/2} = \frac{[A_0]}{2k}$
$A \longrightarrow$ product	1	Rate = k [A]	$k = \frac{2.303}{t}\log\left[\frac{A_0}{A}\right]$	$t_{1/2} = \frac{0.693}{k}$
$2A \longrightarrow$ product	2	Rate = $k[A]^2$	$k = \frac{1}{t}\left[\frac{1}{A} - \frac{1}{A_0}\right]$	$t_{1/2} \propto \frac{1}{[A_0]}$

Effect of Temperature on Rate of Reactions

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

$$\text{Temperature coefficient } (n) = \frac{K_t + 10}{K_t} = 2$$

Arrhenius Equation

Arrhenius equation is purely an empirical equation that gives a reasonably good representation of temperature dependence of the rate constant.

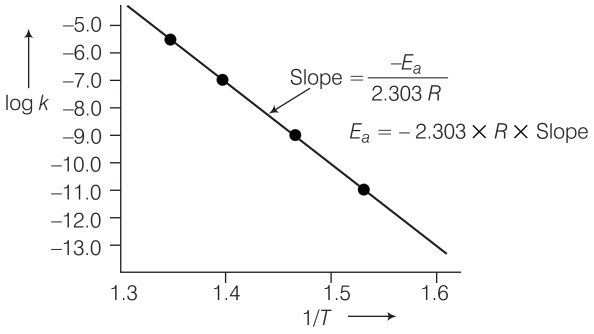
When log k is plotted against $1/T$, we get a straight line which is represented by Arrhenius equation as

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

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

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

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

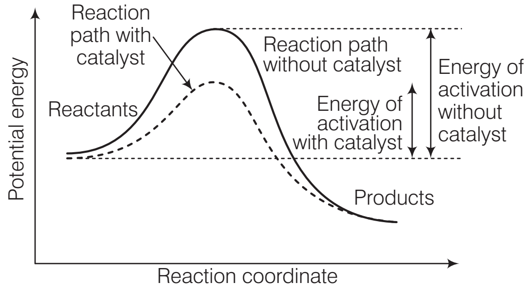


A plot between log k and $1/T$

Activation Energy

- It is the minimum additional energy required by the molecule to attain threshold energy.
- It is constant for a particular reaction.
- It 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



Effect of catalyst on activation energy

- 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.

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 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

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

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

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

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

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

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

This relation is used when rate constants at two different temperatures are given.

- This reaction is also written as $\dfrac{d \log k}{dT} = \dfrac{E_a}{RT^2}$

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 For the reaction, $2A + B \longrightarrow$ Products; the active mass of B is kept constant, and that of A is doubled. The rate of reaction will be

(a) decrease 4 times
(b) decrease 2 times
(c) increase 4 times
(d) increase 2 times

2 In a reaction $A + B \longrightarrow$ product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled. Rate law for the reaction can be written as **→ CBSE-AIPMT 2012**

(a) Rate $= k[A][B]^2$
(b) Rate $= k[A]^2[B]^2$
(c) Rate $= k[A][B]$
(d) Rate $= k[A]^2[B]$

3 For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ the rate of change of concentration for hydrogen is 0.3×10^{-4} Ms^{-1}.

The rate of change of concentration of ammonia is

(a) -0.2×10^{-4} (b) 0.2×10^{-4}
(c) 0.1×10^{-4} (d) 0.3×10^{-4}

4 For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, if $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol $L^{-1}s^{-1}$, the value of $\frac{-d[H_2]}{dt}$ would be **→ CBSE AIPMT 2009**

(a) 3×10^{-4} mol L^{-1} s^{-1} (b) 4×10^{-4} mol L^{-1} s^{-1}
(c) 6×10^{-4} mol L^{-1} s^{-1} (d) 1×10^{-4} mol L^{-1} s^{-1}

5 For the reaction, $A + B \longrightarrow$ products, it is observed that

I. On doubling the initial concentration of A only, the rate of reaction is also doubled.

II. On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is, given by **→ CBSE AIPMT 2009**

(a) rate $= k[A]^2[B]$
(b) rate $= k[A][B]^2$
(c) rate $= k[A]^2[B]^2$
(d) rate $= k[A][B]$

6 The rate law for the chemical reaction

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2 \text{ is}$$

rate $= k[NO_2Cl]$. The rate determining step is

(a) $2NO_2Cl \longrightarrow 2NO_2 + 2Cl$
(b) $NO_2 + Cl_2 \longrightarrow NO_2Cl + Cl$
(c) $NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$
(d) $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$

7 Given, the hypothetical reaction mechanism

$A \xrightarrow{\text{I}} B \xrightarrow{\text{II}} C \xrightarrow{\text{III}} D \xrightarrow{\text{IV}} E$ and the rate as

Species formed	Rate of its formation
B	0.002 mol/h per mole of A
C	0.030 mol/h per mole of B
D	0.011 mol/h per mole of C
E	0.420 mol/h per mole of D

The rate determining step is

(a) step I (b) step II (c) step III (d) step IV

8 For the reaction, $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ the experimental data suggest, rate $= k[H_2][Br_2]^{1/2}$

The molecularity and order of the reaction respectively are

(a) $1, \frac{1}{2}$ (b) 1, 1
(c) $\frac{3}{2}, \frac{3}{2}$ (d) $2, \frac{3}{2}$

9 What is the order of a reaction which has following rate expression? rate $= k[A]^{3/2}[B]^{-1}$

(a) $\frac{3}{2}$ (b) $\frac{1}{2}$ (c) 0 (d) None of these

10 Mechanism of a hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ is given below

(i) $X_2 \rightleftharpoons X + X$(fast) (ii) $X + Y_2 \longrightarrow XY + Y$(slow)
(iii) $X + Y \longrightarrow XY$ (fast)

The overall order of the reaction will be **→ NEET 2017**

(a) 1 (b) 2 (c) 0 (d) 1.5

11 Which one of the following statements for the order of a reaction is incorrect? **→ CBSE-AIPMT 2011**

(a) Order is not influenced by stoichiometric coefficient of the reactants
(b) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction
(c) Order of reaction is always whole number
(d) Order can be determined only experimentally

12 For a reaction between A and B, the initial rate of reaction is measured for various initial concentrations of A and B. The data provided are

	$[A]$	$[B]$	Initial reaction rate
(1)	0.20 M	0.30 M	5×10^{-5}
(2)	0.20 M	0.10 M	5×10^{-5}
(3)	0.40 M	0.05 M	1×10^{-4}

The overall order of the reaction is

(a) one (b) two
(c) two and half (d) three

13 If a certain reaction is first order with respect to A, second order with respect to B and zero order with respect to C then what is the order of reaction?

(a) First (b) Second (c) Third (d) Zero

14 When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is → **CBSE-AIPMT 2014**

(a) zero (b) first
(c) second
(d) more than zero but less than first

15 When initial concentration of the reactant is doubled, the half-life period of a zero order reaction → **NEET 2018**

(a) is tripled (b) is doubled
(c) is halved (d) remains unchanged

16 For a reaction $aA \longrightarrow xP$, when $[A] = 2.2$ mM, the rate was found to be 2.4 m Ms^{-1}.
On reducing concentration of A to half, the rate changes to 0.6 m Ms^{-1}. The order of reaction with respect to A is

(a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

17 In the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, initial pressure is 500 atm and rate constant k is $3.38 \times 10^{-5} s^{-1}$. After 10 min, the final pressure of N_2O_5 is

(a) 490 atm (b) 250 atm (c) 480 atm (d) 420 atm

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

(a) 1.023 M (b) 0.8725 M
(c) 0.023 M (d) 0.1576 M

19 Half-life period of a first order reaction is 1386s. The specific rate constant of the reaction is → **CBSE-AIPMT 2009**

(a) $5.0 \times 10^{-3} s^{-1}$ (b) $0.5 \times 10^{-2} s^{-1}$
(c) $0.5 \times 10^{-3} s^{-1}$ (d) $5.0 \times 10^{-3} s^{-1}$

20 The correct difference between first and second- order reactions is that → **NEET 2018**

(a) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
(b) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
(c) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
(d) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations

21 For a first order reaction, the concentration changes from 0.8 to 0.4 in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is

(a) 30 min (b) 15 min (c) 7.5 min (d) 60 min

22 After how many seconds will the concentration of the reactant in a first order reaction be halved, if the rate constant is 1.155×10^{-3} s^{-1}?

(a) 600 (b) 100 (c) 60 (d) 10

23 The concentration of reactant X decreases from 0.1 M to 0.005 M in 40 min. If the reaction follows first order kinetics, the rate of reaction when concentration of X is 0.01 M will be

(a) 1.73×10^{-4} M min^{-1} (b) 3.47×10^{-4} M min^{-1}
(c) 3.47×10^{-5} M min^{-1} (d) 7.50×10^{-4} M min^{-1}

24 The rate of first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

(a) 0.383 min (b) 23.1 min (c) 8.73 min (d) 7.53 min

25 The rate constant of a zero order reaction is 0.2 mol dm^{-3} h^{-1}. If the concentration of the reactant after 30 min is 0.05 mol dm^{-3}. Then, its initial concentration would be

(a) 0.01 mol dm^{-3} (b) 0.15 mol dm^{-3}
(c) 0.25 mol dm^{-3} (d) 4.00 mol dm^{-3}

26 The half-life period for zero order reaction $A \longrightarrow$ Product; is 100 min. How long will it take in 80% completion?

(a) 80 min (b) 160 min
(c) 100 min (d) 200 min

27 The value of rate constant of a pseudo first order reaction

(a) depends on the concentration of reactants present in small amount
(b) depends on the concentration of reactants present in excess
(c) is independent of the concentration of reactants
(d)depends only on temperature

28 Which of the following statements is in accordance with collision theory?

(i) Rate is directly proportional to collision frequency.
(ii) Rate depends upon orientation of atoms.
(iii) Temperature determines the rate.

(a) Only (iii) (b) (i) and (ii) (c) (ii) and (iii) (d) All of these

29 When we increase temperature, the rate of reaction increase because of

(a) more number of collisions
(b) decrease in mean free path
(c) more number of energetic collisions
(d) less number of energetic collisions

30 In a zero order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10° C to 100°C, the rate of the reaction will become → **CBSE-AIPMT 2012**

(a) 256 times (b) 512 times (c) 64 times (d) 128 times

31 The temperature coefficient of most of the reactions lies between

(a) 1 and 3 (b) 2 and 3 (c) 1 and 4 (d) 2 and 4

32 The activation energy of a reaction is 9 kcal/mol. The increase in the rate constant when its temperature is raised from 295 to 300 K is approximately

(a) 10% (b) 50% (c) 100% (d) 29%

33 What is the activation energy for a reaction if its rate doubles when temperature is raised from 20°C to 35°C? ($R = 8.314\ \text{J}^{-1}\ \text{K}^{-1}$) **→ NEET 2013**

(a) 269 kJ mol^{-1}
(b) 34.7 kJ mol^{-1}
(c) 15.1 kJ mol^{-1}
(d) 342 kJ mol^{-1}

34 The activation energy of a reaction can be determined from the slope of which of the following graphs? **→ CBSE-AIPMT 2015**

(a) $\ln k$ vs T (b) $\frac{\ln k}{T}$ vs T (c) $\ln k$ vs $\frac{1}{T}$ (d) $\frac{T}{\ln k}$ vs $\frac{1}{T}$

35 For a reversible reaction, $A \rightleftharpoons B$, which one of the following statements is wrong from the given energy profile diagram?

(a) Activation energy of forward reaction is greater than backward reaction
(b) The forward reaction is endothermic
(c) The threshold energy is less than that of activation energy
(d) The energy of activation of forward reaction is equal to the sum of heat of reaction and the energy of activation of backward reaction

36 The rate constant is doubled when temperature increases from 27° C to 37° C. Activation energy in kJ is

(a) 34
(b) 54
(c) 100
(d) 53

37 A reaction having equal energies of activation for forward and reverse reaction has **→ NEET 2013**

(a) $\Delta G = 0$
(b) $\Delta H = 0$
(c) $\Delta H = \Delta G = \Delta S = 0$
(d) $\Delta S = 0$

38 For the two gaseous reactions, following data are given

$$A \longrightarrow B;\ k_1 = 10^{10} e^{-20,000/T}$$
$$C \longrightarrow D;\ k_2 = 10^{12} e^{-24,606/T}$$

the temperature at which k_1 becomes equal to k_2 is

(a) 400 K (b) 1000 K (c) 800 K (d) 1500 K

39 In the presence of a catalyst, activation energy of a reaction lowered by 2 kcal at 27°C. Hence, rate will be

(a) 20 times
(b) 28 times
(c) 14 times
(d) remain the same

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 A drop of solution (volume = 0.05 mL) contains 60.0×10^{-7} mol of H^+. If the rate of disappearance of H^+ is 6.0×10^5 mol / Ls, how long time will it take for H^+ to disappear from the drop?

(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 $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$, If $-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k_1[\text{N}_2\text{O}_5]$, $\frac{\Delta[\text{NO}_2]}{\Delta t} = k_2[\text{N}_2\text{O}_5]$, $\frac{\Delta[\text{O}_2]}{\Delta t} = k_3[\text{N}_2\text{O}_5]$, then

(a) $k_1 = k_2 = k_3$
(b) $2k_1 = k_2 = 4k_3$
(c) $2k_1 = 4k_2 = k_3$
(d) None of these

3 For the reaction, $A(g) + 2B(g) \longrightarrow C(g) + D(g)$;

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

Initial pressure of A and B are respectively 0.60 atm and 0.80 atm. At a time when pressure of C is 0.20 atm, rate of the reaction, relative to the initial value is

(a) $\frac{1}{6}$
(b) $\frac{1}{48}$
(c) $\frac{1}{4}$
(d) $\frac{1}{24}$

4 In the complex reaction,

$$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$$
$$\left(\frac{dx}{dt}\right) = 1 \times 10^2 \text{M}^{-3}[\text{N}_2][\text{H}_2]^3 - 1 \times 10^{-3}\text{M}^{-1}[\text{NH}_3]^2$$
$$\frac{[\text{N}_2]\,[\text{H}_2]^3}{[\text{NH}_3]^2} = 10^{-5}\ \text{M}^{-2},\ \text{if}\ \left(\frac{dx}{dt}\right)\ \text{is}$$

(a) 0 (b) 1×10^5 (c) 1×10^{-5} (d) 1×10^{-3}

5 The reaction $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$ is of first order. If volume of reaction vessel is reduced to 1/3, the rate of reaction would be

(a) 1/3 times (b) 2/3 times (c) 3 times (d) 6 times

6 At a certain temperature, the first order rate constant, k_1 is found to be smaller than the second order rate constant, k_2. If the energy of activation, E_1 of the first order reaction is greater than energy of activation, E_2 of the second order reaction then with increase in temperature

(a) k_1 will increase faster than k_2, but always will remain less than k_2
(b) k_2 will increase faster than k_1
(c) k_1 will increase faster than k_2 and becomes equal to k_2
(d) k_1 will increase faster than k_2 and becomes greater than k_2

7 The rate law for a reaction between the substances A and B is given by rate $= k[A]^n[B]^m$. On doubling, the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(a) $\frac{1}{2^{m+n}}$ (b) $(m+n)$

(c) $(n-m)$ (d) $2^{(n-m)}$

8 The rate constant for the reaction,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

is 2.3×10^{-2} s^{-1}. Which equation given below describes the change of $[N_2O_5]$ with time?

($[N_2O_5]_0$ and $[N_2O_5]_t$ corresponds to the concentration of N_2O_5 initially and at time t)

(a) $[N_2O_5]_t = [N_2O_5]_0 + kt$

(b) $[N_2O_5]_0 = \log [N_2O_5]_t + kt$

(c) $\log[N_2O_5]_t = \log [N_2O_5]_0 + kt$

(d) $\ln \frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$

9 For a zero order reaction, the rate constant is equals to 0.025 ms^{-1} for the disappearance of A. What will be the concentration of A after 15s, if the initial concentration is 0.50 M?

(a) 0.375 M (b) 0.125 M

(c) 0.060 M (d) 0.50 M

10 $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ th of its initial value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as

(a) $0.75/k$ (b) $0.69/k$

(c) $0.29/k$ (d) $0.10/k$

11 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 $1/T$ is linear.

Select the correct statement.

(a) I, II and III (b) Both I and III

(c) Both II and III (d) Both I and II

12 For a chemical reaction, $A \longrightarrow$ products, it is found that the rate increases by a factor of 6.25, when the concentration of A is increased by a factor of 2.5. The order of reaction with respect to A is

(a) 2 (b) 0.5 (c) 1 (d) 2.5

13 A reactant (X) forms two products

$X \longrightarrow Y$, Activation energy E_{a_1}, rate constant, $= k_1$

$X \longrightarrow Z$, Activation energy E_{a_2}, rate constant, k_2

If, $E_{a_2} = 2E_{a_1}$, then k_1 with k_2 will be related as

(a) $k_1 = 2k_2 e^{\frac{-Ea_2}{RT}}$ (b) $k_2 = k_1, e^{\frac{-Ea_2}{RT}}$

(c) $k_2 = k_1 e^{\frac{-Ea_1}{RT}}$ (d) $k_1 = Ak_2 e^{\frac{-Ea_1}{RT}}$

14 For a first order reaction, the plot of $\log k$ against $1/T$ is a straight line. The slope of the line is equal to

(a) $-\frac{2.303}{E_a R}$ (b) $\frac{-E_a}{2.303R}$ (c) $\frac{-E_a}{R}$ (d) $\frac{-E_a}{2.303}$

15 The half-life of the reaction;

$$N_2O_5 \longrightarrow 2NO + \frac{1}{2}O_2;\ \text{is 2.4 h.}$$

Starting with 10.8 g of N_2O_5. How much oxygen will be obtained after period of 9.6 h?

(a) 1.5 L (b) 3.36 L (c) 1.05 L (d) 0.07 L

ANSWERS

SESSION 1	**1** (c)	**2** (d)	**3** (b)	**4** (a)	**5** (b)	**6** (d)	**7** (a)	**8** (d)	**9** (b)	**10** (d)
	11 (c)	**12** (a)	**13** (c)	**14** (b)	**15** (b)	**16** (b)	**17** (a)	**18** (d)	**19** (c)	**20** (b)
	21 (a)	**22** (a)	**23** (d)	**24** (b)	**25** (b)	**26** (b)	**27** (b)	**28** (d)	**29** (c)	**30** (b)
	31 (b)	**32** (d)	**33** (b)	**34** (c)	**35** (c)	**36** (d)	**37** (b)	**38** (b)	**39** (b)	
SESSION 2	**1** (b)	**2** (b)	**3** (a)	**4** (a)	**5** (c)	**6** (a)	**7** (d)	**8** (d)	**9** (b)	**10** (c)
	11 (a)	**12** (a)	**13** (c)	**14** (b)	**15** (c)					

Hints and Explanations

SESSION 1

1 $2A + B \longrightarrow$ products

It is a third order reaction.

Rate of reaction, $r_1 = k[A]^2[B]$

If the concentration of A become double then the rate will be

$$r_2 = k[2A]^2[B]$$

$$r_2 = 4k[A]^2[B]$$

$$r_2 = 4r_1$$

2 Let the order of reaction with respect to A and B is x and y respectively, So the rate law can be given as

$$R = k[A]^x[B]^y. \quad ..(i)$$

When the concentration of only B is doubled, the rate is doubled , so

$$R_1 = k[A]^x[2B]^y = 2R \quad ...(ii)$$

If concentration of both the reactants A and B are doubled the rate increases by a factor of 8, so

$$R'' = k[2A]^x[2B]^y = 8R \quad ...(iii)$$

$$\Rightarrow \quad k2^x2^y[A]^x[B]^y = 8R \quad ...(iv)$$

From Eqs. (i) and (ii), we get

$$\Rightarrow \frac{2R}{R} = \frac{[A]^x[2B]^y}{[A]^x[B]^y}, \quad 2 = 2^y \Rightarrow y = 1$$

From Eqs. (i) and (iv), we get

$$\Rightarrow \frac{8R}{R} = \frac{2^x2^y[A]^x[B]^y}{[A]^x[B]^y} \text{ or } 8 = 2^x2^y$$

Substitution of the value of y gives,
$8 = 2^x2^1$, $4 = 2^x \Rightarrow (2)^2 = (2)^x$
$\Rightarrow x = 2$
Substitution of the value of x and y in Eq. (i) gives,

$$R = k[A]^2[B]$$

3 $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$-\frac{d[H_2]}{dt} = -0.3 \times 10^{-4}\ \text{Ms}^{-1}$$

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

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

$$= -\frac{2}{3} \times (0.3 \times 10^{-4}) = 0.2 \times 10^{-4}$$

4 For the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

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

$$= +\frac{1}{2}\frac{d[NH_3]}{dt}$$

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

$$-\frac{d[H_2]}{dt} = \frac{3}{2} \times 2 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

$$= 3 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

5 For the reaction,

$$A + B \longrightarrow \text{Products}$$

On doubling the initial concentration of A only, the rate of the reaction is also doubled, therefore

$$\text{Rate} \propto [A]^1 \quad ...(i)$$

Let initial rate law is

$$\text{Rate} = k[A][B]^y \quad ...(ii)$$

If concentration of A and B both are doubled, the rate gets changed by a factor of 8.

$$8 \times \text{rate} = k[2A][2B]^y \quad ...(iii)$$

$$[\because \text{Rate} \propto [A]^1]$$

Dividing Eq. (iii) by Eq. (ii), we get

$$8 = 2 \times 2^y \Rightarrow 4 = 2^y$$

$$(2)^2 = (2)^y \quad \Rightarrow y = 2$$

Hence, rate law is, rate $= k[A][B]^2$

6 Rate $= k[NO_2Cl]$

Hence, rate determining step is

$$2NO_2Cl \longrightarrow 2NO_2 + 2Cl$$

7 The slowest step is the rate determining step. Formation of B (i.e. step I) is the slowest step, therefore step I is the rate determining step.

8 For the reaction,

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Rate of reaction $= k[H_2][Br_2]^{1/2}$

Molecularity of reaction $= 1 + 1 = 2$

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

9 Rate $= k\,[A]^{3/2}[B]^{-1}$

Order of reaction $= \frac{3}{2} + (-1) = \frac{1}{2} = 0.5$

10 We know that, slowest step is the rate determining step.

$$\therefore \text{Rate } (r) = k_1[X][Y_2] \quad ...(i)$$

Now, from equation. (i), i.e.

$$X_2 \rightarrow 2X \text{ [fast] ;} \qquad k_{eq} = \frac{[X]^2}{[X_2]}$$

$$[X] = \{k_{eq}[X_2]\}^{1/2} \quad ...(ii)$$

Now, substitute the value of $[X]$ from Eq. (ii) in Eq. (i), we get

Rate $(r) = k_1(k_{eq})^{1/2}[X_2]^{1/2}[Y_2]$

$$= k[X_2]^{1/2}[Y_2]$$

$\therefore$ Order of reaction $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5$

11 Order of reaction may be zero, whole number or fraction number. Thus, statement 'C' is incorrect.

12 If the order of reaction w.r.t A is n and the order of reaction w.r.t B is m, rate law becomes

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

From Eq. (i),

$$5 \times 10^{-5} = [0.20]^n\,[0.30]^m \quad ...(i)$$

From Eq. (ii),

$$5 \times 10^{-5} = [0.20]^n\,[0.10]^m \quad ...(ii)$$

From Eq. (iii),

$$1 \times 10^{-4} = [0.40]^n\,[0.05]^m$$

$$10 \times 10^{-5} = [0.40]^n\,[0.05]^m \quad ...(iii)$$

From Eqs. (i) and (ii),

$$\frac{5 \times 10^{-5}}{5 \times 10^{-5}} = \left[\frac{0.20}{0.20}\right]^n \left[\frac{0.30}{0.10}\right]^m$$

$$1 = (3)^m \Rightarrow (3)^0 = (3)^m \Rightarrow m = 0$$

From Eqs. (ii) and (iii),

$$\frac{5 \times 10^{-5}}{10 \times 10^{-5}} = \left[\frac{0.20}{0.40}\right]^n \left[\frac{0.10}{0.05}\right]^m$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n \times \left(\frac{0.10}{0.05}\right)^0$$

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

Overall order of the reaction

$$= n + m = 1 + 0 = 1$$

13 Rate law, $\frac{dx}{dt} = k[A]^1[B]^2[C]^0$

$$= k[A]^1[B]^2$$

Hence, overall order of reaction

$$= 1 + 2 = 3.$$

14 For a zero order reaction, $t_{1/2}$ is directly proportional to the initial concentration of the reaction,

$$[R]_0\, t_{1/2} \propto [R]_0$$

For a first order reaction,

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

at $t_{1/2}$, $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

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

$$t_{1/2} = \frac{2.303}{k} = \log 2 = \frac{2.303}{k} \times .3010$$

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

i.e. half-life period is independent of initial concentration of a reactant.

15 For zero order reaction, $t_{1/2} = \frac{[R]_0}{2k}$

where, $[R]_0$ = Initial concentration of the reactant.

k = Rate constant.

Thus, $t_{1/2}$ for zero order reaction is directly proportional to the initial concentration of the reactant.

$$t_{1/2} \propto [R]_0$$

∴ For zero order reaction, when the concentration of reactant is doubled, the half-life ($t_{1/2}$) will also get doubled.

16 $aA \longrightarrow xP$

Rate of reaction = $k\,[A]^a$

When $[A_1] = 2.2$ mM, $r_1 = 2.4$ m Ms^{-1}

When $[A_2] = \frac{2.2}{2}$ mM, $r_2 = 0.6$ m Ms^{-1}

$$\frac{r_1}{r_2} = \frac{k[A_1]^a}{k[A_2]^a} \quad \text{or} \quad \frac{2.4}{0.6} = \left(\frac{2.2}{1.1}\right)^a \quad \text{or}$$

$4 = (2)^a$

∴ $a = 2$

∴ Order of reaction is 2.

17 From the unit of rate constant (i.e. s^{-1}), it is clear that the reaction is of first order.

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

Hence, for first order reaction,

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

$$\therefore\ 3.38 \times 10^{-5} = \frac{2.303}{10 \times 60} \log \frac{500}{p_t}$$

or $\log \frac{500}{p_t} = 0.00880$

$$\therefore\ \frac{500}{p_t} = \text{antilog}\ (0.00880) = 1.02$$

$$p_t = \frac{500}{1.02} = 490 \text{ atm}$$

18 For first order reactions,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0\text{ h})}$$

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

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

$$\log \frac{[A]_0}{[A]} = \frac{0.693}{3\text{ h}} \times \frac{(8\text{ h})}{2.303} = 0.8024$$

$$\frac{[A]_0}{[A]} = \text{Antilog}\ (0.8024) = 6.345$$

$$[A]_0 = 1\text{ M}; [A] = \frac{[A]_0}{6.345} = \frac{1\text{ M}}{6.345}$$

$$= 0.1576\text{ M}$$

After 8 h, sucrose left = 0.1576 M

19 Specific rate constant,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386} = 0.5 \times 10^{-3}\ \text{s}^{-1}$$

20 For first order reactions, the rate of reaction is proportional to the first power of the concentration of the reactant .

For, $A \rightarrow B$

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

[where, k = constant]

$$\text{Half-life}\ (t_{1/2}) = \frac{0.693}{k}$$

∴ Rate of first order reaction depends upon reactant concentrations and half life does not depend upon initial concentration of reactant, $[A]_0$.

For second order reactions, the rate of reaction is proportional to the second power of the concentration of the reactant.

For, $2A \rightarrow B$ Rate = $k[A]^2$

$$\text{Half-life}\ (t_{1/2}) = \frac{1}{k[A]_0}$$

∴ Rate of second order reaction depends upon reactant concentration and half life also does depend on $[A]_0$.

21 Order = 1

Concentration changes from 0.8 M to 0.4 M (50%) in 15 min, thus half-life is 15 min. A change from 0.1 M to 0.025 M is 75% and for first order reaction

$$T_{75} = 2 \times T_{50} = 2 \times 15 = 30 \text{ min}$$

22 Rate constant $k = 1.155 \times 10^{-3}\ \text{s}^{-1}$

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

$$\left(\text{Here, } a = a, (a-x) = \frac{a}{2}\right)$$

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

$$= \frac{2.303}{1.155 \times 10^{-3}} \log 2$$

$$= \frac{2.303}{1.155 \times 10^{-3}} \times 0.3010$$

$$= \frac{0.693 \times 10^{3}}{1.155} = 600\text{ s}$$

Alternatively,

$$t_{1/2} = \frac{0.6093}{k} = \frac{0.693}{1.155 \times 10^{-3}}$$

$$= 600\text{ s}$$

23 $k = \frac{2.303}{t} \log \frac{A_0}{A}$

$$= \frac{2.303}{40} \log \frac{0.1}{0.005} = 0.075$$

∴ Rate of reaction = $k\,[X]$

$$= 0.075 \times 0.01 = 7.50 \times 10^{-4}\ \text{M min}^{-1}.$$

24 ∵ Rate, $\left(\frac{dx}{dt}\right) = k[A]$

$$\therefore\ 1.5 \times 10^{-2} = k \times 0.5$$

$$k = \frac{1.5 \times 10^{-2}}{0.5}$$

$$= 3 \times 10^{-2}\ \text{min}^{-1}$$

For a first order reaction,

Half-life period,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}}$$

$$= 23.1\text{ min}$$

25 For zero order reaction,

$$x = kt = 0.2\ \text{mol dm}^{-3}\text{h}^{-1} \times \frac{30}{60}\ \text{h}$$

$$= 0.1\ \text{mol dm}^{-3}$$

Concentration = 0.05 mol dm^{-3}

Hence, initial concentration

$$= 0.1 + 0.05 = 0.15\ \text{mol dm}^{-3}$$

26 For zero order reaction,

$$k = \frac{a}{2t_{1/2}} = \frac{a}{2 \times 100} = \frac{a}{200}$$

When 80% completion take place,

$$k = \frac{x\ \ a}{t\ 200} = \frac{0.80a}{t}$$

$$t = 200 \times 0.8 = 160\text{ min}$$

27 Rate constant of pseudo 1st order reaction only depends on the concentration of reactants present in excess.

Like, $RCl + H_2O \longrightarrow ROH + HCl$

Rate $= k\,[RCl]\,[H_2O]$

Actual rate law, Rate $= k\,[RCl]$

28 According to collision theory,

(i) The reaction rate depends on collision frequency and effective collisions. For a molecule to have effective collisions it should fulfill two conditions; proper orientation and sufficient energy.

(ii) Greater the temperature, greater will be the collision rate.

29 Rate of reaction increases with increase in temperature because the number of energetic collision increases.

30 For 10° rise in temperature, $n = 1$

so, rate $= 2^n = 2^1 = 2$

When temperature is increased from 10°C to 100°C, change in temperature $= 100 - 10 = 90$°C, i.e. $n = 9$

So, rate $= 2^9 = 512$ times

Alternate method, with every 10° rise in temperature rate becomes double,

$$\text{so } \frac{r'}{r} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512 \text{ times}$$

31 Temperature coefficient is the ratio of two velocity constant having the difference of 10°C. For most of the reaction, the value of temperature coefficient lies between 2 and 3.

32
$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log\frac{k_2}{k_1} = \frac{9000}{2.303 \times 2}\left(\frac{300 - 295}{295 \times 300}\right)$$

$$\log\frac{k_2}{k_1} = 0.1103 \qquad \frac{k_2}{k_1} = 1.288$$

$$k_2 = 1.288\,k_1$$

i.e. increase by 28.8%.

33
$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{293} - \frac{1}{308}\right]$$

$$0.3 = \frac{E_a}{2.303 \times 8.314} \times \frac{15}{293 \times 308}$$

$$E_a = 34.7 \text{ kJ/mol}$$

34 By Arrhenius equation

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

where, E_a = energy of activation

Applying log on both the side,

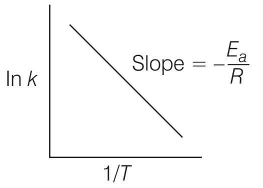
$$\ln k = \ln A - \frac{E_a}{RT} \qquad \ldots\text{(i)}$$

$$\text{or } \log k = -\frac{E_a}{2.303RT} + \log A \qquad \ldots\text{(ii)}$$

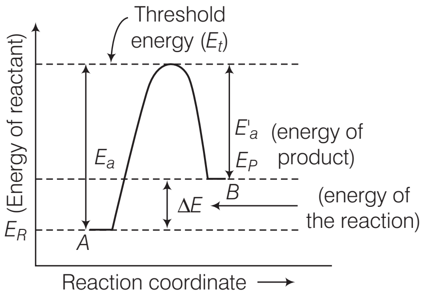
This equation is of the form of $y = mx + c$, i.e. the equation of a straight line. Thus, if a plot of $\log k$ vs $\frac{1}{T}$ is a straight line, the validity of the equation of confirmed.

$$\text{Slope of the line} = -\frac{E_a}{2.303R}$$

Thus, measuring the slope of the line, the value of E_a can be calculated.



35



where, E_a = activation energy of forward reaction

E_a' = activation energy of backward reaction

The above energy profile diagram shows that $E_a > E'_a$

The potential energy of the product is greater than that of the reactant, so the reaction is endothermic.

$$E_a = E'_a + \Delta E$$

$$E_t = E_a \text{ or } E_t > E'_a$$

36 We know,

Given, $T_1 = 27 + 273 = 300$ K $\quad k_1 = k$

$T_2 = 37 + 273 = 310$ K $\quad k_2 = 2k$

$R = 8.314 \times 10^{-3}$ kJ

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

$$2.303\log\frac{2k}{k} = \frac{E_a}{8.314 \times 10^{-3}} \times \left(\frac{310 - 300}{310 \times 300}\right)$$

$$2.303\log 2 = \frac{E_a}{8.314 \times 10^{-3}} \times \frac{10}{93000}$$

$$2.303 \times 0.3010 = \frac{E_a}{8.314 \times 10^{-3}} \times \frac{10}{93000}$$

$$E_a = \frac{2.303 \times 0.3010 \times 8.314 \times 10^{-3}}{10} \times 93000$$

$$E_a = 53.363 \text{ kJ} \simeq 53 \text{ kJ}$$

37 $\Delta H = (E_a)_{\substack{\text{forward}\\ \text{reaction}}} - (E_a)_{\substack{\text{backward}\\ \text{reaction}}} = 0; \quad \Delta H = 0$

38 Given, $k_1 = 10^{10}e^{-20,000/T}$

$$k_2 = 10^{12}e^{-24,606/T}$$

$$k_1 = k_2$$

$$10^{10}e^{-20,000/T} = 10^{12}e^{-24,606/T}$$

$$e^{\frac{-20,000}{T} + \frac{24,606}{T}} = 10^2$$

$$e^{\frac{4,606}{T}} = 10^2$$

On taking log both sides,

$$\frac{4606}{2.303T} = \log 10^2$$

$$2\log 10 \times T = \frac{4606}{2.303}$$

$$T = \frac{4606}{2.303 \times 2} = \frac{4606}{4.606} = 1000 \text{ K}$$

39 Arrhenius equation is

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

In the presence of catalyst,

rate constant $k' = Ae^{-E_a'/RT}$

Eq. (ii)/Eq. (i), we get

$$\frac{k'}{k} = e^{(E_a/E'_a)/RT}$$

$$\frac{k'}{k} = e^{\left(\frac{2000}{2 \times 300}\right)} = e^{3.33}$$

$$[\because E_a - E_a' = 2000 \text{ cal (given)}]$$

$\because$ On taking log both sides,

$$\log\frac{k'}{k} = \frac{3.33}{2.303}$$

$$\frac{k'}{k} = \text{antilog } 1.446$$

$$= 27.92 \approx 28$$

We know that, rate $(R) \propto k$

$$\therefore \quad \frac{R'}{R} = \frac{k'}{k} = 28$$

or $\quad R' = 28R$

SESSION 2

1 $[H^+] = \dfrac{6.0 \times 10^{-7} \text{mol}}{5.0 \times 10^{-5}\ \text{L}} = 1.2 \times 10^{-2}\ \text{M}$

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

$$= \frac{1.2 \times 10^{-2}\ \text{M}}{6.0 \times 10^{5}\ \text{m/s}} = 2.0 \times 10^{-8}\ \text{s}$$

2 Based on the given reaction,

$$-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\frac{k_1}{2}[N_2O_5] = \frac{k_2}{4}[N_2O_5] = k_3[N_2O_5]$$

$$\therefore \quad 2k_1 = k_2 = 4k_3$$

3 $\left(\dfrac{dx}{dt}\right)_0 = k(0.60)(0.80)^2 = 0.384\,k$

$$\begin{array}{cccc} A(g) & + \; 2B(g) & \longrightarrow \; C(g) & + \; D(g) \\ 0.60 & 0.80 & 0 & 0 \\ (0.60 - x) & (0.80 - 2x) & x & x \end{array}$$

$$x = 0.2 \text{ atm}$$

$$\therefore \quad [A] = 0.4 \text{ atm}$$

$$[B] = 0.4$$

$$\therefore \quad \left(\frac{dx}{dt}\right)_t = k(0.4)(0.4)^2 = 0.064\,k$$

$$\therefore \quad \left(\frac{dx}{dt}\right)_t \Big/ \left(\frac{dx}{dt}\right)_0 = \frac{0.064k}{0.384k} = \frac{1}{6}$$

4 $N_2 + 3H_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2NH_3$

$$\left(\frac{dx}{dt}\right)_{\text{net}} = k_f[N_2][H_2]^3 - k_b[NH_3]^2$$

$$\text{Also, } \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{k_f}{k_b}$$

$$\text{or } \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{k_b}{k_f} = \frac{1 \times 10^{-3}}{1 \times 10^{2}}$$

$$= 1 \times 10^{-5}$$

$$\left(\frac{dx}{dt}\right) = 1 \times 10^{2} \text{M}^{-3} \times 10^{-5}[NH_3]^2 - 1 \times 10^{-3}[NH_3]^2$$

$$\text{Thus, } \left(\frac{dx}{dt}\right) = 0$$

5 $2NO(g) + O_2 \longrightarrow 2NO_2(g)$

When the volume of vessel changes into $\frac{1}{3}$, then concentration of reactant becomes three times. The rate of reaction for first order reaction is directly proportional to concentration, Therefore, rate of reaction will increases three times.

6 $\dfrac{d[\ln k]}{dt} = \dfrac{E_a}{RT^2}$

As E_a increases, rate constant,k also increases so k_1 will increase faster than k_2 but always will remain less than k_2.

7 Rate becomes x^y times, if concentration is made x times of a reactant giving yth order reaction.

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

Concentration of A is doubled hence $x = 2$, $y = n$ and rate becomes $= 2^n$ times.

Concentration of B is halved, hence $x = \frac{1}{2}$ and $y = m$ and rate becomes

$$= \left(\frac{1}{2}\right)^m \text{ times.}$$

$$\text{Net rate becomes} = (2)^n\left(\frac{1}{2}\right)^m \text{ times}$$

$$= (2)^{n-m} \text{ times}$$

8 From the unit of rate constant (s^{-1}). It is clear that the reaction is of first order. For a first order reaction,

$$k = \frac{1}{t}\log_e \frac{a}{a-x} \Rightarrow kt = \log_e \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

9 $\dfrac{dx}{dt} = k = 0.025\ \text{ms}^{-1}$

$$\text{or } \frac{x}{t} = k = 0.025\,\text{ms}^{-1}$$

$$x = 15 \times 0.025 = 0.375\ \text{M}$$

Thus, $[A] = 0.50 - 0.375 = 0.125$ M

10

$$\begin{array}{lcc} & A \longrightarrow & \text{Product} \\ \text{Initially} & a & 0 \\ \text{After time, } t & (a - x) & x \\ \text{After, } t_{1/4} & \left(a - \frac{a}{4}\right) & \frac{a}{4} \end{array}$$

For the first order kinetics,

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

$$\therefore \quad k = \frac{2.303}{t_{1/4}}\log\frac{a}{\frac{3a}{4}}$$

$$t_{1/4} = \frac{2.303\log\frac{4}{3}}{k} = \frac{0.29}{k}$$

11 $\log k\ (\text{min}^{-1}) = 5 - \dfrac{2000\ \text{K}}{T}$

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

I. $\log_{10} A = 5$,

$A = 10^5$, true

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

$$E_a = 2000 \times 2.303 \times 0.002 \text{ kcal}$$

$$= 9.212 \text{ kcal, true}$$

III. Equation represents straight line, hence true,

12 Rate, $R = k\,[A]^m$ or $6.25R = k\,[2.5A]^m$

$$\therefore \quad 6.25 = (2.5)^m \text{ or } (2.5)^2 = (2.5)^m$$

$$\therefore \quad m = 2$$

The order of reaction with respect to A is 2.

13 $\because\ k \propto e^{-E_a/RT}$ (Arrhenius equation)

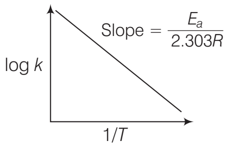
$$\text{or } k = Ae^{\frac{-E_a}{RT}} \quad k_1 = Ae^{-E_{a_1}/RT}$$

$$\text{and } k_2 = Ae^{\frac{-E_{a_2}}{RT}} \quad \text{but, } E_{a_2} = 2E_{a_1}$$

$$\therefore k_2 = Ae^{\frac{-2E_{a_1}}{RT}} = Ae^{\frac{-E_{a_1}}{RT}} \cdot e^{\frac{-E_{a_1}}{RT}}$$

$$k_2 = k_1 e^{\frac{-E_{a_1}}{RT}}$$

14 $\log k = \log A \dfrac{-E_a}{2.303R} \times \dfrac{1}{T}$



15 $N_2O_5 \longrightarrow 2NO + \frac{1}{2}O_2$

$$\text{Moles of } N_2O_5 = \frac{10.8}{108} = 0.1$$

$$\text{Number of half-lives} = n = \frac{9.6}{2.4} = 4$$

$$N_t = 0.1 \times \left(\frac{1}{2}\right)^n = (0.1) \times \left(\frac{1}{2}\right)^4 = \frac{0.1}{16}$$

$$\text{Moles of } N_2O_5 \text{ left} = \frac{0.1}{16}$$

Moles of N_2O_5 changed to product

$$= 0.1 - \frac{0.1}{16} = \frac{1.5}{16}$$

$$\text{Volume of } O_2 \text{ formed} = \frac{1.5}{2 \times 16} \times 22.4$$

$$= 1.05 \text{ L}$$