11 Chemical Kinetics

QUICK LOOK

The reactions involving strong bond-breaking occur at relatively slower rate while those involving weak bond–breaking occur at relatively faster rate. On the basis of rate, reactions are classified as.

- Instantaneous or extremely fast reactions *i.e.,* reactions with half-life of the order of fraction of second.
- Extremely slow reactions *i.e.,* reactions with half-life of the order of years.
- Reactions of moderate or measurable rate.

In general, for a reaction, $n_1A + n_2B \longrightarrow m_1C + m_2D$

The rate is expressed as: $-\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = \frac{-1}{n_2}\frac{\Delta[B]}{\Delta t} = \frac{1}{m_1}\frac{\Delta[C]}{\Delta t} = \frac{1}{m_2}\frac{\Delta[D]}{\Delta t}$

Instantaneous Rate With the progress of reaction the conc. of reactants decreases while that of product increases. According to law of mass action the rate of reaction decreases moment to moment as shown by graph of rate vs. time. Rate varies from moment to moment so rate of reaction has to be specified at a given instant of time called instantaneous rate

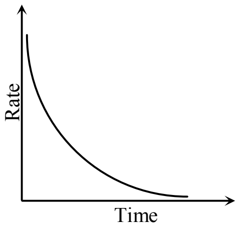


Figure: 11.1

$$r_{ins} \text{ or } r_t = \pm\frac{dC}{dt}$$

Where dC is the infinitesimal change in conc. during infinitesimal time interval dt after time t *i.e.* between t and t + dt.

Consider a reaction $A \longrightarrow B$, To know the rate of reaction at any time t, a tangent is drawn to curve at the point corresponding to that time and it is extended on either side so as to cut the axes, say at the point A and B. Then

$$\text{Rate of reaction} = \frac{\text{Change in the conc.}}{\text{Time}}$$

$$= \frac{\Delta x}{\Delta t} = \frac{OA}{OB} = \text{slope of the tangent}$$

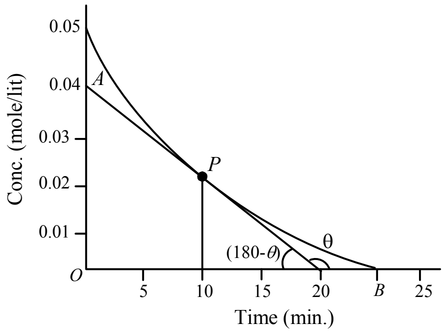


Figure: 11.2

Thus the rate of reaction at time 10 minutes

$\Delta t = 20 \times 60 = 1200\,\text{sec}$.

$\Delta x = 0.04\,\text{moles}$

$$r_{ins} = \frac{0.04}{1200} = 3.35 \times 10^{-5} \text{ mol lit}^{-1} \text{ sec}^{-1}$$

Factors Affecting Rate of a Reaction: The rate of a chemical reaction depends on the following things

Nature of Reactants

- **Physical state of reactants:** This has considerable effect over rate of reaction.

$$\xrightarrow[\text{Decreasing rate of reaction}]{\text{Gaseous satae } > \text{Liquid state} > \text{Solid state}}$$

- **Physical size of the reactants:** Among the solids, rate increases with decrease in particle size of the solid.
- Chemical nature of the reactants:
- Reactions involving polar and ionic substances including the proton transfer reactions are usually very fast. On the other hand, the reaction in which bonds is rearranged, or electrons transferred are slow.
- Oxidation-reduction reactions, which involve transfer of electrons, are also slow as compared to the ionic substance.
- Substitution reactions are relatively much slower.

Effect of Temperature: The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost double or tripled for every 10°C rise in temperature. Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by (generally 25°C and 35°C) 10°C.

$$\mu = \text{Temperature coefficient} = \frac{k \text{ at } (t+10^\circ C)}{k \text{ at } t^\circ C} = \frac{k_{35^\circ C}}{k_{25^\circ C}}$$

Concentration of Reactants: The rate of a chemical reaction is directly proportional to the concentration of the reactants means rate of reaction decreases with decrease in concentration.

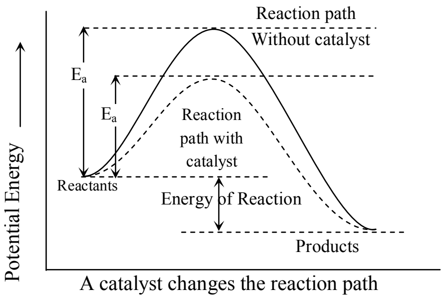


Figure: 11.3

Presence of Catalyst: The function of a catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate.

Effect of Sunlight: There are many chemical reactions whose rate are influenced by radiations particularly by ultraviolet and visible light. Such reactions are called photochemical reactions. For example, Photosynthesis, Photography, Blue printing, Photochemical synthesis of compounds etc. The radiant energy initiates the chemical reaction by supplying the necessary activation energy required for the reaction.

Rate Law: Molecularity and Order of a Reaction: Molecularity is the sum of the number of molecules of reactants involved in the balanced chemical equation. Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. Slowest step is the rate-determining step. This was proposed by Van't Hoff.

Example: $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Unimolecular)

$NO + O_3 \longrightarrow NO_2 + O_2$ (Bimolecular)

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

The total number of molecules or atoms whose concentration determine the rate of reaction is known as order of reaction. Order of reaction = Sum of exponents of the conc. terms in rate law. For the reaction $xA + yB \longrightarrow \text{Products}$

The rate law is Rate = $[A]^x [B]^y$

Then the overall order of reaction. $n = x + y$

Where x and y are the orders with respect to individual reactants.

If reaction is in the form of reaction mechanism then the order is determined by the slowest step of mechanism.

$2A + 3B \longrightarrow A_2B_3$

$A + B \longrightarrow AB$ (fast)

$AB + B_2 \longrightarrow AB_3$ (slow) (Rate determining step)

$AB_3 + A \longrightarrow A_2B_3$ (fast)

(Here, the overall order of reaction is equal to two.)

Molecularity of a reaction is derived from the mechanism of the given reaction. Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

- Molecularity of a reaction can't be zero, negative or fractional. Order of a reaction may be zero, negative, positive or in fraction and greater than three. Infinite and imaginary values are not possible.
- When one of the reactants is present in the large excess, the second order reaction conforms to the first order and is known as pesudo unimolecular reaction.

Pseudo First Order Reaction: Reaction whose actual order is different from that expected using rate law expression is called pseudo – order reactions, *eg.*

$RCl + H_2O \longrightarrow ROH + HCl$

Expected rate law:

Rate = K[RCl] [H_2O], Expected order = 1+1 = 2

Actual rate law: Rate = K' [RCl], Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. This reaction is therefore, pseudo first order. Similarly, the acid catalysed hydrolysis of ester, *viz,*

$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$

Follows first order kinetics.

Rate = K [RCOOR']

It is also a pseudo – first order reaction.

Difference between Order and Molecularity

- Order is an experimental property while molecularity is the theoretical property.
- Order concerns with kinetics (rate law) while molecularity concerns with mechanism.
- Order may be any number, fraction, integral or even zero whereas molecularity is always an integer expecting zero.

Reactions of Various Orders

Zero Order Reactions: A reaction is said to be zero order if its rate is independent of the conc. of the reactants, consider the general reactions: $A \longrightarrow \text{Products}$

If it is reac. of zero order

$$\text{Rate} = \frac{-d[A]}{dt} = K[A]^o = K \text{ or } d[A] = -K\,dt$$

Integrating both sides, we get $[A] = -Kt + I$ . . .(*i*)

Where I is a constant of integration At $t = 0, [A] = [A]_o$

$\therefore \quad [A]_o = I$

Substituting this value of I in equation (*i*), we get

$$[A] = -Kt + [A]_o \qquad ...(ii)$$

or $\quad Kt = [A]_o - [A] \quad K = \frac{1}{t}\left\{[A]_o - [A_t]\right\}$

Some important characteristics of reaction of zero order.

- Any reaction of zero order must obey equation
- As it is a equation of straight line (y = mx+c), the plot of [A] versus t will be a straight line with slope = – K and intercept on the conc. axis = $[A]_o$ as shown in figure

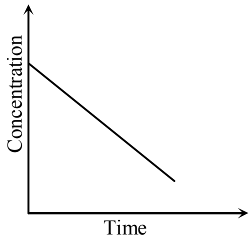


Figure: 11.4

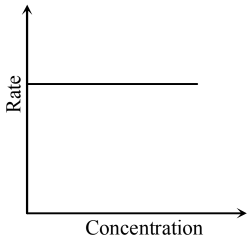


Figure: 11.5

Half reaction period: Half life period ($t_{1/2}$) is the time in which half of the substance has reacted. When [A] = $\frac{[A_o]}{2}$, $t = t_{1/2}$ substituting those values in equation (iii), we get

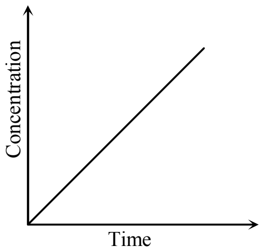


Figure: 11.6

$$t_{1/2} = \frac{1}{K}\left[[A]_o - \frac{[A]_o}{2}\right] = \frac{[A]_o}{2K} \quad t_{1/2} = \frac{[A]_o}{2K}$$

Unit of K: $K = \frac{\text{molar conc.}}{\text{Time}} = \frac{\text{mol L}^{-1}}{\text{time}} = \text{mole L}^{-1}\ \text{time}^{-1}$

First order Reaction: A reaction is said to be of the first order if the rate of the reaction depends upon one conc. term only. Consider the reaction

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

Let 'a' be the conc. of A at the start and after time t, the conc. becomes (a – x), *i.e.,* x has been changed into products. The rate of reaction after time 't' is given by the expression

$$\frac{dx}{dt} = K(a-x) \quad \text{or} \quad \frac{dx}{(a-x)} = K\,dt$$

Upon integration of above equation, $\int \frac{dx}{(a-x)} = K\int dt$

or $\quad -\log_e(a-x) = Kt + c$

Where c is integration constant when $t = 0, x = 0$

$\therefore \quad c = -\log_e a$

Putting the value of 'c', $-\log_e(a-x) = Kt - \log_e a$

or $\quad \log_e a - \log_e(a-x) = Kt$

$$\log_e \frac{a}{(a-x)} = Kt$$

$$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

If the initial concentration is $[A_o]$ and the concentration after time t is [A], then putting a = $[A]_o$ and $(a-x) = [A]$, equation becomes

$$K = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$

This equation can be written in the exponential form as

$$\frac{[A]_o}{[A]_t} = e^{kt} \text{ or } \frac{[A]}{[A]_o} = e^{-Kt} \text{ or } [A] = [A]_o\, e^{-Kt}$$

Some Complex First Order Reactions: Parallel Reactions in such reactions (mostly organic) a single reactant gives two products B and C with different rate constants. If we assume that both of them are first order, we get.

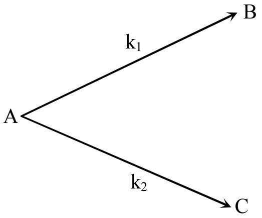


Figure: 11.7

$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A] \qquad ...(i)$$

$$\frac{d[B]}{dt} = k_1[A] \qquad ...(ii)$$

and $\quad \frac{d[C]}{dt} = k_2[A] \qquad ...(iii)$

Let us assume that in a time interval, dt, x moles / lit of B was produced and y moles/lit of C was produced.

$\therefore \quad \frac{d[B]}{dt} = \frac{x}{dt}$ and $\frac{d[C]}{dt} = \frac{y}{dt}$

$\therefore \quad \frac{d[B]/dt}{d[C]/dt} = \frac{x}{y}$

We can also see that from (*ii*) and (*iii*), $\frac{d[B]/dt}{d[C]/dt} = \frac{k_1}{k_2}$

$$\therefore \quad \frac{x}{y} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2.

Sequential Reactions: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. In this A decomposes to B which in turn decomposes to C.

$$\therefore \quad \frac{-d[A]}{dt} = k_1[A] \qquad \ldots(i)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \ldots(ii)$$

$$\frac{d[C]}{dt} \; k_2[B] \qquad \ldots(iii)$$

$$\therefore \quad t_{max} = \frac{1}{K_1 - K_2} \text{In} \frac{K_1}{K_2} \qquad \ldots(iv)$$

Substituting equation (iv) in equation (iii), we get

$$B_{max} = B_{max} = [A]_o \left[\frac{k_2}{k_1}\right]^{k_2/k_1 - k_2}$$

Concept of Activation Energy

The excess energy (Over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called activation energy (E_a),

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactants})}$$

Activation energy = Threshold energy–Average kinetic energy of the reacting molecules.

- Zero activation energy = Fraction of effective collision (f) will be very large = Very fast reaction (Instantaneous reaction).
- Low activation energies = Fraction of effective collision (f) will be large = Fast reactions.
- High activation energies = Fraction of effective collision (f) will be small = Slow reaction.

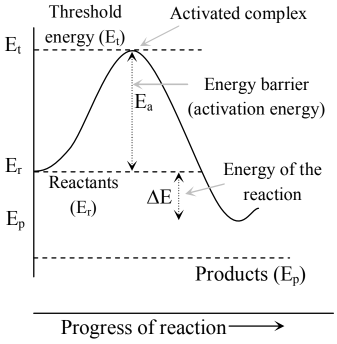


Figure: 11.8

The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. According to the concept of activation energy, the reactants do not change directly into the products. The reactant first absorbs energy equal to activation energy and form activated complex. At this state, the molecules must have energy at least equal to the threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as activation energy barrier.

Transition State Theory

- According to transition state theory the activated complex is supposed to be in equilibrium with the reactant molecules.
- Once the transition state is formed it can either return to the initial reactants or proceeds to form the products.
- Assuming that once formed the transition state proceeds to products we can say that rate is proportional to concentration of transition state.
  Mathematically, Rate $\propto$ Transition state
  Rate = Constant × Transition state
- The activation energy for the forward reaction, (E_a^f) and the activation energy for the reverse reaction (E_a^r) are related to the enthalpy (ΔH) of the reaction by the equation $\Delta H = E_a^f - E_a^r$.
  (a) For endothermic reactions, $\Delta H > 0$, so that $E_a^r < E_a^f$
  (b) For exothermic reaction, $\Delta H < 0$, so that $E_a^r > E_a^f$.

Arrhenius Equation: The variation of equilibrium constant of a reaction with temperature is described by Van't Hoff equation of thermodynamics which is as follows:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

If k_1 and k_2 be the rate constants of forward reaction and backward reaction, respectively then $K_p = k_1/k_2$.

Further, $\Delta H = Ea_1 - Ea_2$.

Putting these in the above equation we get,

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{E_{a_1}}{RT^2} - \frac{E_{a_2}}{RT^2}$$

Splitting into two parts

$$\frac{d \ln k_1}{dT} = \frac{E_{a_1}}{RT^2} + Z \quad (\text{For FR})$$

$$\frac{d \ln k_2}{dT} = \frac{E_{a_2}}{RT^2} + Z \quad (\text{For BR})$$

Where Z is constant

Arrhenius sets Z equal to zero and without specifying FR and BR, he gave the following equation called Arrhenius equation.

$$\frac{d\ln k}{dT}=\frac{Ea}{RT^2} \qquad \ldots(i)$$

From this equation it is evident that rate of change of logarithm of rate constant with temperature depends upon the magnitude of energy of activation of the reaction. Higher the Ea smaller the rate of change of logarithm of rate constant with temperature. That is, rate of the reaction with low E_a increases slowly with temperature while rate of the reaction with high E_a increases rapidly with temperature. It is also evident that rate of increase of logarithm of rate constant will go on decreasing with increase of temperature.

Integrating Equation 4 assuming Ea to be constant we get,

$$\ln\ k=-\frac{Ea}{RT}+\ln A \qquad \ldots(ii)$$

$$\text{or } \ln\frac{k}{A}=-\frac{Ea}{RT} \quad \text{or } k=Ae^{-Ea/RT} \qquad \ldots(iii)$$

Equation (iii) is integrated form of Arrhenius equation. The constant A called pre-exponential factor is the frequency factor since it is somewhat related with collision frequency. It is a constant for a given reaction. From Equation (iii) it is evident that as $T\to\propto, K\to A$. Thus, the constant A is the rate constant of reaction at infinity temperature. The rate constant goes on increasing with temperature. So, when T approaches infinity, k will be maximum. That is to say, A is the maximum rate constant of a reaction. It is also to be noted that the exponential term *i.e.* $e^{-Ea/RT}$ measures the fraction of total number of molecules in the activated state or fraction of the total number of effective collisions. If n_{Ea} and n be the number of molecules of reactant in the activated state and the total number of molecules of the reactant present in the reaction vessel respectively, then $\frac{n_{E_a}}{n}=e^{-E_a/RT}$

Equation (*ii*) may also be put as logk

$$=\left(-\frac{Ea}{2.303R}\right)\frac{1}{T}+\log A \qquad \ldots(iv)$$

Since $\frac{E_a}{2.303R}$ and logA both are constants for a given reaction.

So from equation (*iv*) it is evident that a plot of log k vs. $\frac{1}{T}$ will be a straight line of the slope equal to

$-\frac{E_a}{2.303R}$ and intercept equal to log A as shown below.

$$\frac{-E_a}{2.303R}=\tan\theta=-\tan(180-\theta)=-\frac{0A}{OB}$$

$$\therefore E_a=\frac{OA}{OB}\times 2.303R \quad \log A=OA$$

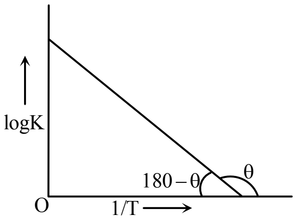


Figure: 11.9

Thus, from this plot E_a and A both can be determined accurately. If k_1 be the rate constant of a reaction at two different temperatures T_1 and T_2 respectively then from equation (*iv*), we may write

$$\log k_1=-\frac{E_a}{2.303R}.\frac{1}{T_1}+\log A$$

$$\text{and } \log k_2=-\frac{E_a}{2.303R}.\frac{1}{T_2}+\log A$$

Subtracting former from the latter we get

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad \ldots(v)$$

With the help of this equation it is possible to calculate E_a of a reaction provided, rate constants of reaction at two different temperatures are known. Alternatively one can calculate rate constant of a reaction at a given temperature provided that rate constant of the reaction at some other temperature and also E_a of the reaction is known.

$$^{230}_{90}\text{Th}^{*}\longrightarrow{}^{230}_{90}\text{Th}+\gamma \qquad (\gamma-\text{emission})$$

Mechanism of the Reaction

Reaction Involving First Order Consecutive Reactions

- In such reactions, the reactions form a stable intermediate compound before they are finally converted into the products.
- For example, reactants (R)are first converted to intermediate (I) which is then converted to product (P) as

$$R\xrightarrow{k_1}I\xrightarrow{k_2}P$$

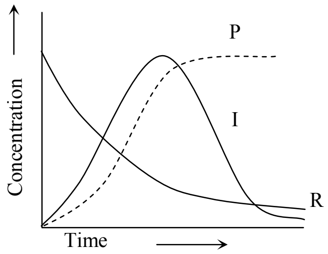


Figure 11.10: Concentration profile of reactants (R), intermediate (I) and products (P) as a function of time

Therefore, the reaction takes place in two steps, both of which are first order *i.e.,*

Step (i): $R\xrightarrow{k_1}I$; **Step (ii):** $I\xrightarrow{k_2}P$

This means that I is produced by step (i) and consumed by step (ii). In these reactions, each stage will have its own rate and rate constant the reactant concentration will always decrease and product concentration will always increase as shown in fig.

Reaction Involving Slow Step: When a reaction occurs by a sequence of steps and one of the step is slow, then the rate determining step is the slow step. For example in the reaction

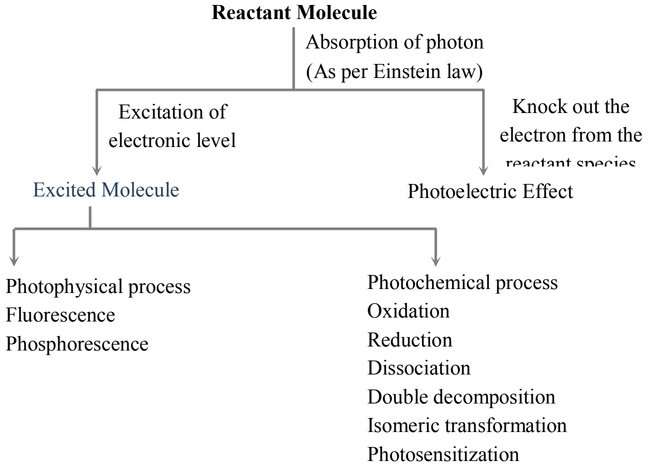
$$R \xrightarrow{k_1} I; \quad I \xrightarrow{k_2} P,$$

If $k_1 << k_2$ then I is converted into products as soon as it is formed, we can say that

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

Photochemical Reaction

Absorption of radiant energy by reactant molecules brings in photo-physical as well as photochemical changes. According to Einstein's law of photochemical equivalence, the basic principle of photo processes, each reactant molecule is capable of absorbing only one photon of radiant energy. The absorption of photon by a reactant molecule may lead to any of the photo process.



The chemical reactions, which are initiated as a result of absorption of light, are known as photochemical reactions. In such cases, the absorbed energy is sufficient to activate the reactant molecules to cross the energy barrier existing between the reactants and products or in other words, energy associated with each photon supplies activation energy to reactant molecule required for the change.

(i) Characteristics of Photochemical Reactions

- Each molecule taking part in a photo process absorbs only one photon of radiant energy thereby increasing its energy level by $h\nu$ or $\frac{hc}{\lambda}$
- Photochemical reactions do not occur in dark. The rate of photochemical reactions depend upon the intensity of radiation's absorbed.
- Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon. For example, reactions needing more energy are carried out in presence of UV light (lower λ, more E/Photon). A reaction-taking place in UV light may not occur on exposure to yellow light (lower λ and lesser E/Photon)
- The ΔG values for light initiated reactions may or may not be negative.

(ii) Mechanism of Some Photochemical Reactions

- Photochemical combination of H_2 and Cl_2: A mixture of H_2 and Cl_2 on exposure to light give rise to the formation of HCl, showing a chain reaction and thereby producing 10^6 to 10^8 molecules of HCl per photon absorbed.

  $$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$$

  The mechanism leading to very high yield of HCl as a result of chemical change can be as follows.

  Light absorption step: $Cl_2 \xrightarrow{h\nu} Cl_2^*$ . . .(*i*)

  Chain initiation step: $Cl_2^* \longrightarrow Cl^\bullet + Cl^\bullet$ . . .(*ii*)

  The chlorine free radical then combines with H_2 molecule to form HCl and $H^\bullet$ free radical. The $H^\bullet$ free radical so formed again combines with another Cl_2 molecule to give HCl and $Cl^\bullet$ free radical back resulting into chain propagation step.

  Chain propagation step:

  $Cl^\bullet + H_2 \longrightarrow HCl + H^\bullet$ . . .(*iii*)

  $H^\bullet + Cl_2 \longrightarrow HCl + Cl^\bullet$

  The combination of two $Cl^\bullet$ free radicals leads to chain terminating step.

  Chain terminating step:

  ` $Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$ . . .(*iv*)

(iii) Quantum Yield (or quantum efficiency)**:** The quantum efficiency or yield (ϕ) of a photochemical reaction may be expressed as,

$$\phi = \frac{\text{No. of molecules reacted or product formed}}{\text{No. of photon absorbed}}$$

(iv) Application of Photochemistry

- Photosynthesis in plants
- Photography
- The formation and destruction of ozone layer
- Photoetching in electronic industry
- Many polymerization reactions.

MULTIPLE CHOICE QUESTIONS

Rate of Reaction

1. For a given reaction $3A + B \longrightarrow C + D$ the rate of reaction can be represented by:

a. $-\frac{1}{3}\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt}$

b. $-\frac{1}{3}\frac{d[A]}{dt} = \frac{d[C]}{dt} = K[A]^m[B]^n$

c. $+\frac{1}{3}\frac{d[A]}{dt} = \frac{-d[C]}{dt} = K[A]^n[B]^m$

d. None of these

2. For the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ if $\frac{\Delta[NH_3]}{\Delta t} = 2\times10^{-4} mol l^{-1} s^{-1}$, the value of $\frac{-\Delta[H_2]}{\Delta t}$ would be:

a. $1\times10^{-4} mol\ l^{-1}s^{-1}$
b. $3\times10^{-4} mol\ l^{-1}s^{-1}$
c. $4\times10^{-4} mol\ l^{-1}s^{-1}$
d. $6\times10^{-4} mol l^{-1}s^{-1}$

3. A gaseous hypothetical chemical equation $2A \rightleftharpoons 4B + C$ is carried out in a closed vessel. The concentration of B is found to increase by $5\times10^{-3} mol\ l^{-1}$ in 10 second. The rate of appearance of B is:

a. $5\times10^{-4} mol\ l^{-1} sec^{-1}$
b. $5\times10^{-5} mol\ l^{-1} sec^{-1}$
c. $6\times10^{-5} mol\ l^{-1}\ sec^{-1}$
d. $4\times10^{-4} mol l^{-1}\ sec^{-1}$

4. The rate of a reaction that not involves gases is not dependent on:

a. Pressure
b. Temperature
c. Concentration
d. Catalyst

5. The concentration of a reactant decreases from 0.2 M to 0.1 M in 10 minutes. The rate of the reaction is:

a. 0.01 M
b. 10^{-2}
c. 0.01 mol $dm^{-3}\ min^{-1}$
d. 1 mol $dm^{-3}\ min^{-1}$

6. If doubling the concentration of a reactant `A' increases the rate 4 times and tripling the concentration of `A' increases the rate 9 times, the rate is proportional to:

a. Concentration of `A'
b. Square of concentration of `A'
c. Under root of the concentration of `A'
d. Cube of concentration of `A'

7. In a catalytic conversion of N_2 to NH_3 by Haber's process, the rate of reaction was expressed as change in the concentration of ammonia per time is $40\times10^{-3} mol litre^{-1}s^{-1}$. If there are no side reaction, the rate of the reaction as expressed in terms of hydrogen is: (in $mol\ litre^{-1}s^{-1}$)

a. 60×10^{-3}
b. 20×10^{-3}
c. 1.200
d. 10.3×10^{-3}

8. If the concentration of the reactants is increased, the rate of reaction:

a. Remains unaffected
b. Increases
c. Decreases
d. May increase or decrease

9. For reaction $2A + B \longrightarrow$ products, the active mass of B is kept constant and that of A is doubled. The rate of reaction will then:

a. Increase 2 times
b. Increase 4 times
c. Decrease 2 times
d. Decrease 4 times

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

a. 1/10
b. 1/8
c. 8
d. 16

11. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is $0.001 kg\,h^{-1}$. The rate of conversion of H_2 under the same conditions is:

a. $1.82\times10^{-4} kg/hr$
b. $0.0015 kg/hr$
c. $1.52\times10^{4} kg/hr$
d. $1.82\times10^{-14} kg/hr$

12. The term $\left(-\frac{dc}{dt}\right)$ in a rate equation refers to the:

a. Concentration of the reactant
b. Decrease in concentration of the reactant with time
c. Increase in concentration of the reactant with time
d. Velocity constant of the reaction

13. Consider the following reversible chemical reactions:

$$A_2(g) + Br_2(g)\ K_1 \xrightleftharpoons{K_1} 2AB(g)$$

$$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 3B_2(g)$$

he relation between K_1 and K_2 is :

a. $K_2 = K_1^3$
b. $K_2 = K_1^{-3}$
c. $K_1K_2 = 3$
d. $K_1K_2 = \frac{1}{3}$

14. The velocity of the chemical reaction doubles every $10^{o}C$ rise of temperature. If the temperature is raised by $50^{o}C$, the velocity of the reaction increases to about:

a. 32 times
b. 16 times
c. 20 times
d. 50 times

15. The temperature coefficient of a reaction is:

a. Specific reaction rate at 25°C

b. Rate of the reaction at 100°C

c. Ratio of the rate constants at temperatures 35°C and 25°C

d. Ratio of the rate constants at two temperatures differing by 1°C

16. The velocity constant of a reaction at 290 K was found to be 3.2×10^{-3}. At 300 K it will be:

a. 1.28×10^{-2}

b. 6.4×10^{-3}

c. 9.6×10^{-3}

d. 3.2×10^{-4}

17. Rate of reaction:

a. Decreases with increase in temperature

b. Increases with increase in temperature

c. May increase or decrease with increase in temperature

d. Does not depend on temperature

18. A first order reaction complete its 10% in 20 minutes then time required to complete its 19% is:

a. 30 minutes

b. 40 minutes

c. 50 minutes

d. 38 minutes

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

a. 112

b. 512

c. 400

d. 614

20. The rate of a reaction:

a. Increases with increase in temperature

b. Decreases with increase in temperature

c. Does not depend on temperature

d. Does not depend on concentration

Characteristics of First Order Reaction

21. $A+2B\longrightarrow C+D.\text{If}.-\frac{d[A]}{dt}=5\times10^{-4}\,\text{mol}\,l^{-1}s^{-1}1$, then $-\frac{d[B]}{dt}$ is:

a. $2.5\times10^{-4}\,\text{mol}\,l^{-1}s^{-1}$

b. $5.0\times10^{-4}\,\text{mol}\,l^{-1}s^{-1}$

c. $2.5\times10-3\text{mol}\,l^{-1}s^{-1}$

d. $1.0\times10^{-3}\,\text{mol}\,l^{-1}s^{-1}$

22. The reaction $N_2O_5\,(\text{in}\,CCl_4\,\text{solution})\longrightarrow 2NO_2\,(\text{solution})+\frac{1}{2}O_2\,(g)$ is of first order in N_2O_5 with rate constant $6.2\times10^{-1}s^{-1}$. What is the value of rate of reaction when? $[N_2O_5]=1.25\,\text{mole}\,l^{-1}$

a. $7.75\times10^{-1}\,\text{mole}\,l^{-1}s^{-1}$

b. $6.35\times10^{-3}\,\text{mole}\,l^{-1}s^{-1}$

c. $5.15\times10^{-5}\,\text{mole}\,l^{-1}s^{-1}$

d. $3.85\times10^{-1}\,\text{mole}\,l^{-1}s^{-1}$

23. A reaction that is of the first order with respect to reactant A has a rate constant 6 min^{-1}. If we start with $[A]=0.5\,\text{mol}\,l^{-1}$, when would $[A]$ reach the value 0.05 mol l^{-1}?

a. 0.384 min

b. 0.15 min

c. 3 min

d. 3.84 min

24. For the reaction $2N_2O_5\longrightarrow 4NO_2+O_2$ rate of reaction and rate constant are 1.02×10^{-4} and $3.4\times10^{-5}\,\text{sec}^{-1}$ respectively. The concentration of N_2O_5 at that time will be:

a. 1.732

b. 3

c. 1.02×10^{-4}

d. 3.4×10^{5}

25. The rate law of the reaction $2N_2O_5\longrightarrow 4NO_2+O_2$ is:

a. $r=K[N_2O_5]$

b. $r=K[N_2O_5]^2$

c. $r=K[N_2O_5]^0$

d. $r=K[NO_2]^4[O_2]$

26. In the reaction $A+B\longrightarrow$ Products, if B is taken in excess, then it is an example of:

a. Second order reaction

b. Zero order reaction

c. Pseudounimolecular reaction

d. First order reaction

27. The half life of a first order reaction is 69.35 sec. The value of the rate constant of the reaction is:

a. $1.0s^{-1}$

b. $0.1s^{-1}$

c. $0.01s^{-1}$

d. $0.001s^{-1}$

28. The half life for the reaction $N_2O_5 \rightleftharpoons 2NO_2+\frac{1}{2}O_2$ in 24 hrs at 30ºC. Starting with 10g of N_2O_5 how many grams of N_2O_5 will remain after a period of 96 hours:

a. 1.25 g

b. 0.63 g

c. 1.77 g

d. 0.5 g

29. Which of the following is an example of pseudo unimolecular reaction?

a. $CH_3COOCH_3+H_2O\xrightarrow{H^+}CH_3COOH+CH_3OH$

b. $CH_3COOCH_3+H_2O\xrightarrow{OH^-}CH_3COOH+CH_3OH$

c. $2FeCl_3+SnCl_2\longrightarrow SnCl_4+2FeCl_2$

d. $NaOH+HCl\longrightarrow NaCl+H_2O$

30. Hydrolysis of DDT is a first order reaction; its half life is 10 years. Time to hydrolyse 10 *g* DDT to half is:

a. 100 years **b.** 50 years
c. 5 years **d.** 10 years

31. In a first order reaction, the concentration of the reactant decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is:

a. 7.5 minutes **b.** 15 minutes
c. 30 minutes **d.** 60 minutes

32. For a first order reaction $A \longrightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be $2.0\times10^{-5}\,\text{mol L}^{-1}\text{s}^{1}$. The half life period of the reaction is:

a. 220 s **b.** 30 s
c. 300 s **d.** 347 s

33. The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is:

a. – 1 **b.** – 2
c. 1 **d.** 2

Arrhenius Equation

34. 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.** 50

35. The activation energy of a reaction is zero. The rate constant of this reaction:

a. Increases with increase of temperature
b. Decreases with an increase of temperature
c. Decreases with decrease of temperature
d. Is independent of temperature

36. The rate constant is given by the equation $k = pze^{-E/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly?

a. T **b.** Z **c.** E **d.** P

37. Which one of the following does not represent Arrhenius Equation?

a. $k = Ae^{-E/RT}$

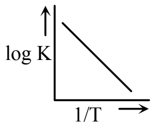
b. $\log_e k = \log_e A - \dfrac{E}{RT}$

c. $\log_{10} k = \log_{10} A - \dfrac{E}{2.303\,RT}$

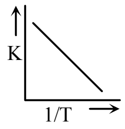
d. $k = AE^{-RT}$

38. Which of the following plots is in accordance with the Arrhenius Equation?

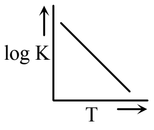
a.



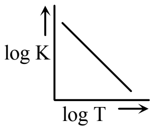
b.



c.



d.



Photochemical Reaction

39. The photolysis of water gives the substance:

a. $OH^- + H^+$ **b.** $H_2 + OH^-$
c. $H_2 + O_2$ **d.** $H_2O + H_2O_2$

40. The law of photochemical equivalence was given by:

a. Drapper **b.** Grauths
c. Einstein **d.** Labbert

Rate Law and Rate Constant

41. The rate law for reaction $A + 2B = C + 2D$ will be:

a. Rate $= K[A][B]$ **b.** Rate $= K[A][2B]$
c. Rate $= K[A][B]^2$ **d.** Rate $= K\dfrac{[C][D]^2}{[A][B]^2}$

42. In the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$, initial pressure is 500atm and rate constant K is $3.38\times10^{-5}\,\text{sec}^{-1}$. After 10 minutes the final pressure of N_2O_5 is:

a. 490 atm **b.** 250 atm
c. 480 atm **d.** 420 atm

43. The reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ 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

44. For a reactions $A + B \longrightarrow$ product, it was found that rate of reaction increases four times if concentration of ‘A’ is doubled, but the rate of reaction remains unaffected. If concentration of ‘B’ is doubled. Hence, the rate law for the reaction is:

a. rate $= k[A][B]$ **b.** rate $= k[A]^2$
c. rate $= k[A]^2[B]^1$ **d.** rate $= k[A]^2[B]^2$

45. In a first order reaction the concentration of reactant decreases from $800\,mol/dm^3$ to $50\,mol/dm^3$ is 2×10^2 sec. The rate constant of reaction in sec^{-1} is:

a. 2×10^4 **b.** 3.45×10^{-5}

c. 1.386×10^{-2} **d.** 2×10^{-4}

46. A reaction that is of the first order with respect to reactant A has a rate constant $6min^{-1}$. If we start with [A] = 0.5 mol l^{-1}, when would [A] reach the value 0.05 mol l^{-1} ?

a. 0.384 min **b.** 0.15 min

c. 3 min **d.** 3.84 min

47. The rate equation for the reaction $2A + B \longrightarrow C$ is found to be: $rate = k[A][B]$. The correct statement in relation to this reaction is that the:

a. Rate of formation of *C* is twice the rate of disappearance of A

b. $t_{1/2}$ is a constant

c. Unit of k must be s^{-1}

d. Value of k is independent of the initial concentrations of A and B

48. The rates of a certain reaction (*dc/dt*) at different times are as follows

Time	Rate (mole litre^{-1} sec $^{-1}$)
0	2.8×10^{-2}
10	2.78×10^{-2}
20	2.81×10^{-2}
30	2.79×10^{-2}

The reaction is:

a. Zero order **b.** First order

c. Second order **d.** Third order

49. A first order reaction which is 30% complete in 30 minutes has a half-life period of:

a. 24.2 *min* **b.** 58.2 *min*

c. 102.2 *min* **d.** 120.2 *min*

50. Diazonium salt decomposes as $C_6H_5N_2^+Cl^- \longrightarrow C_6H_5Cl + N_2$

At 0°C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is:

a. A first order reaction

b. A second order reaction

c. Independent of the initial concentration of the salt

d. A zero order reaction

51. The rate of the reaction

$CCl_3CHO + NO \longrightarrow CHCl_3 + NO + CO$ is given by Rate $= K[CCl_3CHO][NO]$. If concentration is expressed in moles/litre, the units of K are:

a. litre^2 mole^{-2} sec^{-1} **b.** mole litre^{-1} sec^{-1}

c. litre mole^{-1} sec^{-1} **d.** sec^{-1}

52. The rate law of the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is:

a. $r = K[N_2O_5]$ **b.** $r = K[N_2O_5]^2$

c. $r = K[N_2O_5]^0$ **d.** $r = K[NO_2]^4[O_2]$

53. A zero order reaction is one whose rate is independent of:

a. Temperature of the reaction

b. The concentrations of the reactants

c. The concentration of the products

d. The material of the vessel in which the reaction is carried out

54. Which of the following is a first order reaction?

a. $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

b. $2HI \longrightarrow H_2 + I_2$

c. $2NO_2 \longrightarrow 2NO + O_2$

d. $2NO + O_2 \longrightarrow 2NO_2$

55. Which one of the following formula represents a first order reaction?

a. $K = \frac{x}{t}$

b. $K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

c. $K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$

d. $K = \frac{1}{t}\frac{x}{a(a-x)}$

56. By "the overall order of a reaction", we mean:

a. The number of concentration terms in the equation for the reaction

b. The sum of powers to which the concentration terms are raised in the velocity equation

c. The least number of molecules of the reactants needed for the reaction

d. The number of reactants which take part in the reaction

57. A first order reaction requires 30 minutes for 50% completion. The time required to complete the reaction by 75% will be:

a. 45 minutes **b.** 15 minutes
c. 60 minutes **d.** None of these

58. The velocity constant of first order reaction is expressed in the units:
a. Concentration per unit time
b. Time per unit concentration
c. Per unit time
d. Unit time per unit concentration

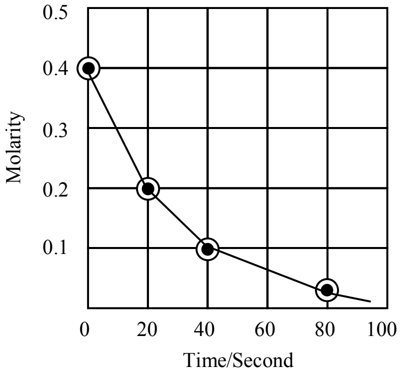
59. For a zero order reaction:
a. The concentration of the reactant does not change during the reaction
b. The concentration change only when the temperature changes
c. The rate remains constant throughout
d. The rate of the reaction is proportional to the concentration

60. Point out the wrong statement:
For a first order reaction
a. Time for half-change ($t_{1/2}$) is independent of initial concentration
b. Change in the concentration unit does not change the rate constant (K)
c. Time for half-change × rate constant = 0.693
d. The unit of K is $\text{mole}^{-1}\ \text{min}^{-1}$

NCERT EXEMPLAR PROBLEMS

More than One Answer

61. A certain reaction $A \longrightarrow B$ follows the given concentration (molarity) time graph. Which of the following statements are correct?

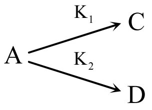


a. The reaction is first order with respect to A
b. The rate of this reaction at 40 sec. will be equal to $3.5\times10^{-3}\ \text{M/sec}$
c. The rate of this reaction at 80 sec. will be equal to $1.75\times10^{-3}\,\text{M/sec}$
d. The [B] will be 0.25 M at 60 sec

62. According to collision theory, not all collisions between molecules lead to reaction. Which of the following statements provide reasons why this is so?
a. The average energy of the two colliding molecules is less than some minimum amount of energy required for the reaction
b. Molecules cannot react with each other unless a catalyst is present.
c. Molecules that are improperly oriented during collision will not react
d. Molecules in different states of matter cannot react with each other

63. $Zn + 2H^{+} \longrightarrow Zn^{2+} + H_2$ Half-life period is independent of concentration of zinc at constant pH. For the constant concentration of zinc, rate becomes 100 time when pH decreases from 3 to 2. Hence:
a. $\frac{dx}{dt} = K\,[Zn]^0[H^+]^2$
b. $\frac{dx}{dt} = K[Zn]^1[H^+]^2$
c. Rate is not effected if concentration of zinc is made four times and that of H^+ ion is halved
d. Rate becomes four times if concentration of H^+ is doubled and concentration of zinc is doubled

64. Consider the following case of competing 1st order reactions after the start of the reaction t = 0 only A, the [C] is equal to [D] at all times. The time in which all three concentrations will be equal is given by:



a. $t = \frac{1}{2k_1}\ln 3$ **b.** $t = \frac{1}{2k_2}\ln 3$
c. $t = \frac{1}{3k_1}\ln 3$ **d.** $t = \frac{1}{3k_2}\ln 3$

65. Which of the following statements are correct?
a. Increase in concentration of reactant increases the rate of zero order reaction
b. Rate constant K is equal to collision frequency A_1 if Ea = 0
c. Rate constant k is equal to collision frequency A_1 if Ea $=\propto$
d. Log K Vs $\frac{1}{T}$ is a straight line

66. $A\,A(qq)+B(aq)\longrightarrow C(aq)$. This reaction is an exothermic following second order kinetics. To increase the rate of the reaction, which of the following can be done?

a. decrease of temperature of the reaction

b. increase of temperature of the reaction

c. increase of concentration of the reactants

d. addition of water to the reaction vessel

67. The reaction $CH_3COOC_2H_5+NaOH\longrightarrow CH_3COONa+C_2H_5OH$ is:

a. Bimolecular reaction

b. II order reaction

c. III order reaction

d. none

68. A reaction is catalysed by 'X'. Here 'X'

a. Decreases the rate constant of reaction

b. Does not affect the equilibrium constant of reaction

c. Decreases the enthalpy of reaction

d. Decreases the activation energy

69. The half-life of a first order reaction having rate constant $K = 1.7 \times 10^{-5}\ s^{-1}$ is:

a. 12.1 h **b.** 9.7 h

c. 11.3 h **d.** 1.8 h

70. Relation between rate constant and temperature by Arrhenius equation is:

a. $\log_e A=\log_e K+\frac{E_a}{RT}$

b. $\log K=A\frac{E_a}{RT}$

c. $\log_e K=\log_e A-\frac{E_a}{RT^2}$

d. $\log A=RT\ln E_a-\ln K$

71. If 'I' is the intensity of absorbed light and C is the concentration of AB for the photochemical process $AB+hv\longrightarrow AB^*$, the rate of formation of AB* is directly proportional to:

a. C **b.** I

c. I^2 **d.** C.I

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

a. If both assertion and reason are true and the reason is the correct explanation of the assertion.

b. If both assertion and reason are true but reason is not the correct explanation of the assertion.

c. If assertion is true but reason is false.

d. If the assertion and reason both are false.

e. If assertion is false but reason is true.

72. **Assertion:** Half-life period of a reaction of first order is independent of initial concentration.
Reason: Half-life period for a first order reaction $t_{1/2}=\frac{2.303}{K}\log 2$.

73. **Assertion:** The photochemical reactions $H_2Cl_2\longrightarrow 2HCl$ and $H_2+Br_2\longrightarrow 2HBr$ have equal quantum efficiencies.
Reason: Both the reactions proceed by similar mechanism.

74. **Assertion:** Vision is not a photochemical reaction.
Reason: Halogenation of alkenes is a photochemical reaction.

75. **Assertion:** Glow worm shows chemiluminescence.
Reason: Glow worm emits light due to oxidation of protein, luciferin present in it.

76. **Assertion:** The rate of reaction is always negative.
Reason: Minus sign used in expressing the rate shows that concentration of product is decreasing.

77. **Assertion:** The kinetic of the reaction $mA+nB+pC\longrightarrow m'X+n'Y+p'Z$ obeys the rate expression as $\frac{dx}{dt}=k[A]^m[B]^n$.
Reason: The rate of the reaction does not depend upon the concentration of C.

78. **Assertion:** Instantaneous rate of reaction is equal to dx/dt.
Reason: It is the rate of reaction at any particular instant of time.

79. **Assertion:** Molecularity has no meaning for a complex reaction.
Reason: The overall molecularity of a complex reaction is equal to the molecularity of the slowest step.

80. **Assertion:** If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.
Reason: For a zero order reaction, the rate of reaction is independent of initial concentration.

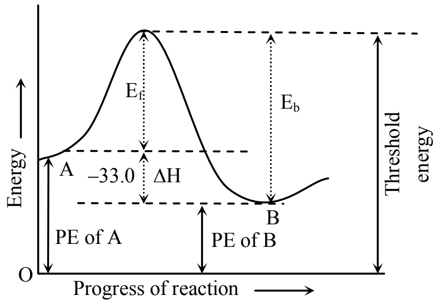
81. **Assertion:** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
Reason: Lower the activation energy, faster is the reaction.

Comprehension Based

Paragraph –I

The energy change accompanying the equilibrium reaction $A \rightleftharpoons B$ is -33.0kJ mol^{-1}.

Assuming that pre-exponential factor is same for forward and backward reaction answer the following



82. The equilibrium constant k for the reaction at 300 K:

a. 5.55×10^5 **b.** 5.67×10^3

c. 5.55×10^6 **d.** 5.67×10^2

83. The energy of activation for forward and backward reactions (E_f and E_b) at 300 K, Given that E_f and E_b are in the ratio 20: 31.

a. 69, 93 **b.** 60, 93

c. 93, 60 **d.** 90, 60

84. The threshold energy of the reaction is when PE of B is 30 kJ mol^{-1}.

a. 130 **b.** 140

c. 123 **d.** 125

Paragraph –II

In the start of summer, a given sample of milk turns sour at room temperature (27ºC) in 48 hours. In a refrigerator at 2ºC, milk can be store three times longer before it sours.

85. The activation energy of the souring of milk is (kJ mol^{-1}):

a. 30.210 **b.** 30.146

c. 30.0 **d.** 35.126

86. The time taken by the milk to sour at 37°C.

a. 35.2 hr **b.** 32.5 hr

c. 35.3 hr **d.** 32.3 hr

87. Calculate the rate constant at 310 K, when rate constant at 300 K is 1.6×10^5 ?

a. 2.363×10^5 **b.** 2.4×10^5

c. 2.450×10^5 **d.** 3.123×10^5

Paragraph –III

Consider the following elementary reactions, $2A + B + C \longrightarrow$ Products. All reactants are present in the gaseous state and reactant C is taken in excess.

88. What is the rate expression of the reaction?

a. Rate $= k[A]^2[B][C]$ **b.** Rate $= k[A]^2[B]$

c. Rate $= k\dfrac{[A]^2[B]}{[C]}$ **d.** Rate $= k[C]^\circ$

89. What is the unit of rate constant of the reaction?

a. $\text{mol L}^{-1} \text{time}^{-1}$ **b.** time^{-1}

c. $\text{mol}^{-1} \text{L}^2 \text{time}^{-1}$ **d.** $\text{mol}^{-2} \text{L}^2 \text{time}^{-1}$

90. How will the rate change if the concentration of A is doubled and that of B is tripled?

a. The rate increases 12 times of original value.

b. The rate increases 8 times of original value.

c. The rate reduces 12 times of original value.

d. The rate reduces 8 times of original value.

Match the Column

91. Match the statement of Column with those in Column II:

Column I	Column II
(A) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$	**1.** Pseudo first order
(B) $CH_3COOC_2H_5 \xrightarrow[H^+ \text{ or } OH^-]{HOH} CH_3COOH + C_2H_5OH$	**2.** Zero order
(C) $H_2 + Cl_2 \xrightarrow{hv} 2HCl$	**3.** Second order
(D) $CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$	**4.** First order

a. A→ 1; B→ 3,4; C→ 2; D→ 3

b. A→ 2; B→ 4; C→ 3; D→1

c. A→ 1; B→ 3,2; C→ 2; D→ 4

d. A→ 4; B→ 1; C→ 3; D→ 2

92. Match the statement of Column with those in Column II:

Column I (Half life)	Column II (Order)
(A) $t_{1/2}$ = constant	**1.** First order
(B) $t_{1/2} \propto a$	**2.** Pseudo first order
(C) $t_{1/2} \propto p^{-1}$	**3.** Zero order
(D) $t_{1/2} \propto 1/a$	**4.** Second order

a. A→ 3,1; B→ 1; C→ 4; D→ 2,3

b. A→ 1,2; B→ 4; C→ 2,3; D→ 1

c. A→ 1,2; B→ 3; C→ 1,2; D→ 3,4

d. A→ 3,4; B→ 1,2; C→ 3; D→ 2

93. Match the statement of Column with those in Column II:

Column I (Kinetic equation)	Column II (Unit of rate constant)
(A) $x = kt$	**1.** $L\,mol^{-1}s^{-1}$
(B) $k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{(a)}\right]$	**2.** s^{-1}
(C) $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$	**3.** $atm^{-1}s^{-1}$
(D) $k = \frac{2.303}{t(a-b)}\log\left[\frac{b(a-x)}{a(b-x)}\right]$	**4.** $mol\,L^{-1}s^{-1}$

a. A→ 4; B→ 1,3; C→ 2; D→ 1,3
b. A→ 2; B→ 3,4; C→ 1,3; D→ 1
c. A→ 1; B→ 2,3; C→ 2; D→ 4
d. A→ 4; B→ 1,3; C→ 3; D→ 2

94. Match the statement of Column with those in Column II:

Column I	Column II
(A) Decomposition of H_2O_2	**1.** $10t_{1/2}$
(B) k_{308}/k_{298}	**2.** (2 to 3) (generally)
(C) $\frac{k}{A} = e^{-E_a/RT}$	**3.** Fractions of collision which are effective
(D) $t_{99.9\%}$ (for first order)	**4.** First order

a. A→ 4; B→ 2; C→ 3; D→ 1
b. A→ 2; B→ 4; C→ 3; D→ 1
c. A→ 1; B→ 3; C→ 2; D→ 4
d. A→ 4; B→ 1; C→ 3; D→ 2

95. Match the statement of Column with those in Column II:

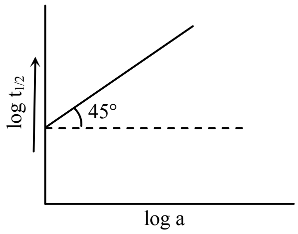
Column I	Column II
(A) Zero order reaction	1. $\frac{k_{t+10}}{k_t} = 2 \text{ or } 3$
(B) First order reaction	2. $2H_2O_2 \longrightarrow 2H_2O + O_2$
(C) Second order reaction	3. $-\frac{dx}{dt} = k[A]^2[B]$
(D) Temperature coefficient	4. $H_2 + Cl_2 \xrightarrow{hv} 2HCl$
	5. $CH_3COOCH_3 + NaOH \longrightarrow CH_3COONa + CH_3OH$

a. A→ 3; B→ 1; C→ 4; D→ 2
b. A→ 4; B→ 2; C→ 5; D→ 1
c. A→ 1; B→ 5; C→ 2; D→ 4
d. A→ 4; B→ 1; C→ 3; D→ 5

Integer

96. Hydrolysis of an alkyl halide (RX) by dilute alkali [OH^-] takes place simultaneously by SN^2 and SN^1 pathways. A plot of $-\frac{1}{[RX]}\frac{d[R-X]}{dt}$ vs [OH^-] is a straight line of the slope equal to 2 × 10^3 mol^{-1} Lh^{-1} and intercept equal to 1 × 10^2 h^{-1} Calculate the intial rate (more $L^{-1}min^{-1}$) of consumption of RX when the reaction is carried out taking 1mol L^{-1} of RX and 0.1 mol L^{-1} of [OH^-] ions:

97. Following is the graph between log $t_{1/2}$ and log *a* (*a* initial concentration) for a given reaction at 27° C Find the order of reaction.



98. In the case of a first order reaction, the time required for 93.75% of reaction to take place is x times that required for half of the reaction. Find the value of x:

99. Following are two first order reactions with their half times given at 25°C.

$A \xrightarrow{t_{1/2}=30\,min} Products$

$B \xrightarrow{t_{1/2}=40\,min} Products$

The temperature coefficients of their reaction rates are 3 and 2, respectively, between 25ºC and 35ºC. If the above two reaction are carried out taking 0.4 M of each reactant but at different temperatures:25ºC for the first order reaction and 35ºC for the second order reaction, find the ratio of the concentrations of A and B after an hour:

100. Consider the following statements for a second order reaction and score of each statement.

$2A \longrightarrow P$

		Score
a.	$[A] = \frac{[A_0]}{1+kt}$	3
b.	A plot of $1/[A]^2$ vs time will be straight line	2
c.	Half life is long when the concentration is low	1

Find the total score of the correct statements:

ANSWER

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**
a	b	a	a	c	b	a	b	b	d
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
b	b	b	a	c	b	c	b	b	a
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
a	a	a	a	a	c	c	b	a	d
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
c	d	b	b	d	c	d	a	a	c
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
c	a	c	b	c	a	d	a	b	a
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
c	a	b	a	c	b	c	c	c	d
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
a,b	a,c	b,c	a,b	b,d	b,c	a,b	d	c	a
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
b	a	d	e	a	d	a	b	b	b
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
b	a	b	c	b	b	a	b	d	a
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
a	c	a	a	b	5	0	4	2	4

SOLUTION

Multiple Choice Questions

1. **(a)** $-\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d(D)}{dt}.$

2. **(b)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\frac{-\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$$\therefore \quad \frac{\Delta[H_2]}{\Delta t} = \frac{3}{2}\times\frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2}\times 2\times10^{-4}$$

$$= 3\times10^{-4}\,\text{mol litre}^{-1}\text{sec}^{-1}$$

3. **(a)** Increase in concentration of $B = 5\times10^{-3}\,\text{mol l}^{-1}$. Time = 10 sec.

$$\text{Rate of appearance of } B = \frac{\text{Increase of conc. B}}{\text{Time taken}}$$

$$= \frac{5\times10^{-3}\,\text{mol l}^{-1}}{10\text{ sec}} = 5\times10^{-4}\,\text{mol l}^{-1}\text{ Sec}^{-1}$$

4. **(a)** The rate of reaction depends upon conc. of reactant, surface area of reactant, temperature, presence of light and catalyst.

5. **(c)** Rate of reaction $= \frac{dx}{dt} = \left[\frac{0.2-0.1}{10}\right] = \frac{0.1}{10}$

$= 0.01$ mol $\text{dm}^{-3}\,min^{-1}$

6. **(b)** $2^2 = 4,\ 3^2 = 9$

7. **(a)** $\frac{-d(N_2)}{dt} = -\frac{1}{3}\frac{d(H_2)}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt}$

$= \frac{3}{2}\times 40\times10^{-3} = 60\times10^{-3}.$

8. **(b)** Greater are the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decreases, the rate of reaction also decreases.

9. **(b)** Rate $= K(A)^2(B)^1$ on doubling the active mass of A the rate of reaction increase 4 times.

10. **(d)** When volume is reduced to $\frac{1}{4}$, concentrations become four times.

11. **(b)** $\frac{-dN_2}{dt} = \frac{-1}{3}\frac{dH_2}{dt} = \frac{1}{2}\frac{dNH_3}{dt}$

$\frac{dH_2}{dt} = \frac{3}{2}\times 0.001 = 0.0015\,\text{kg hr}^{-1}.$

12. **(b)** $-\frac{dc}{dt}$ refers as decrease in concentration of the reactant with time.

13. **(b)** $A_2(g) + B_2(g) \overset{k_1}{\rightleftharpoons} 2AB$ . . .(*i*)

$\Rightarrow$ equation (i) × 3

$6\,AB(g) \rightleftharpoons 3A_2(g) + 3B_2(g)$

$\Rightarrow \left(\frac{1}{k_1}\right)^3 = k_2$

$\Rightarrow k_2 = (k_1)^{-3}$

14. **(a)** $\frac{K_t + 10}{K_t} = \frac{r_t + 10}{r_t} = 2;$

For an increase of temperature to 50°C, *i.e.* 5 times, the rate increases by 2^5 times, *i.e.* 32 times.

15. **(c)** Temperature coefficient $\frac{K_{35^\circ C}}{K_{25^\circ C}} = \frac{K_{308k}}{K_{298k}} = 2$ and 3 for most reactions.

16. **(b)** As we know that the velocity constant become double by increasing the temperature by $10°C$ so if at 290 K, velocity constant $= 3.2\times10^{-3}$ then at 300K, velocity constant $= 2(K_{290}) = 2\times3.2\times10^{-3} = 6.4\times10^{-3}$.

17. **(c)** Rate of reaction may increase or decrease with increase in temperature. If reaction is exothermic, rate decreases with increasing temperature while that of endothermic reactions increase with increasing temperature.

18. **(b)** In first phase, $K = \frac{2.303}{20}\log\frac{90}{100}$ . . . (*i*)

In second phase $K = \frac{2.303}{t}\log\frac{81}{100}$ . . . (*ii*)

From eq. (*i*) $\frac{2.303}{20}\log\frac{90}{100} = \frac{2.303}{t}\log\frac{81}{100}$

$$t = \frac{20(\log 81 - \log 100)}{(\log 90 - \log 100)}$$

$$= \frac{20(1.908-2)}{(1.954-2)} = \frac{20\times(-0.092)}{(-0.046)} = 40 \text{ minutes}$$

19. **(b)** $\frac{k_t + 10}{K_t} = \frac{r_t + 10}{r_t} = 2$

For an increase of temperature to 90°C *i.e.* 9 times, the rate increases by 2^9 times *i.e.* 512.

20. **(a)** Thus both rate and rate constant *K* increase with temperature, $r = k\,(\text{reactant})^n$ and $k = Ae^{-Ea/RT}$.

21. **(a)** $A + 2B \longrightarrow C + D$

$$\frac{-d[A]}{dt} = 5\times10^{-4}$$

$$-\frac{1}{2}\frac{d[B]}{dt} = \frac{5\times10^{-4}}{2} = 2.5\times10^{-4}\,\text{mol}^{-1}\,\text{sec}^{-1}$$

22. **(a)** Rate $= K(N_2O_5) = 6.2\times10^{-1}\times1.25$

$= 7.75\times10^{-1}$ mol l^{-1} s^{-1}

23. **(a)** We know that for first order kinetics

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

$(a-x) = 0.05$ mol l^{-1},

$$6 = \frac{2.303}{t}\log\frac{0.5}{0.05}$$

or $t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6} = 0.384\,\text{min}$

24. **(a)** $R = K[A],\ 1.02\times10^{-4} = 3.4\times10^{-5}, [N_2O_5]$

Or, $(N_2O_5) = \frac{1.02\times10^{-4}}{3.4\times10^{-5}}, K = 3$

25. **(a)** Rate law for the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is $r = k[N_2O_5]$ first order reaction.

26. **(c)** When B is in excess, it becomes a pseudo-unimolecular reaction.

27. **(c)** $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.35} = 9.99\times10^{-3}$

$= 0.01\,s^{-1}$

28. **(b)** $k = \frac{0.693}{24}\,\text{hr}^{-1}$

$$= \frac{2.303}{96}\log\frac{10}{a-x}$$

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

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

or $\log(a-x) = -0.2036 = 1.7964$

or $(a-x) = \text{antilog } 1.7964 = 0.6258\,\text{gm}$

29. **(a)** When in any chemical reaction, one of the reactant is present in large excess, then the second order reaction becomes first order reaction and is known as pseudo unimolecular reaction *e.g.,*

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

in this reaction molecularity is 2 but order of reaction is found to be first order experimentally, so it is an example of pseudo unimolecular reaction.

30. **(d)** $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\,\text{years}}$

If initial concentration a = 10 gm and final concentration

$x = \frac{a}{2} = 5$ gm

Then, $t = \frac{2.303}{K}\log\frac{a}{a-x}$

$$= \frac{2.303}{.693}\times10\times\log\frac{10}{5}$$

$$= \frac{2.303\times10\times\log 2}{.693}$$

$$= \frac{2.303\times10\times0.301}{0.693} = 10 \text{ years.}$$

31. **(c)** The concentration of the reactants decrease from 0.8 to 0.4 in 15 min *i.e.,* $T_{1/2} = 15$ min, concentration from 0.1m to 0.025 will fall in 2 half lives so total time taken $= 2\times T_{1/2} = 2\times15 = 30$ min.

32. **(d)** $R = K[A]$

$2\times10^{-5} = K\times10^{-2}$

$K = 2\times10^{-3}\,\text{sec}^{-1}$

$$t_{1/2} = \frac{.693}{K} = \frac{.693}{2\times10^{-3}} = \frac{693}{2} = 347\,\text{sec}$$

33. **(b)** $R = k[B]^n;\ \frac{1}{4}R = k[2B]^n;$

$$4 = \left(\frac{1}{2}\right)^n;\ 4 = 2^{-n};\ n = -2.$$

34. **(b)** $\log\frac{K_2}{K_1}=\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$

If $\frac{K_2}{K_1}=2$

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

$$E_a=.3010\times 2.303\times 8.314\left(\frac{300\times 310}{10}\right)$$

$$=53598.59\ \text{Jmol}^{-1}=54\ \text{kJ}.$$

35. **(d)** When $E_a=0$, the rate of reaction becomes independent of temperature. (E_a = Energy of activation).

36. **(c)** When k increases, rate of reaction also increases, $k=\frac{pz}{e^{E/RT}}$ for k to increase p, z, T should increase and E should decrease. ($e\approx 2.7$).

37. **(d)** All other are different forms of Arrhenius equation.

38. **(a)** A graph plotted between $\log k$ vs $\frac{1}{T}$ for calculating activation energy.

39. **(a)** $H_2O\xrightarrow{\text{Photolysis}}OH^-+H^+$

40. **(c)** Stark-Einstein was given the law of photo-chemical equivalence.

41. **(c)** The rate law for an reaction can be given by; rate $=K(A)(B)^2$, *i.e.* the powers are raised which are given as coefficient of reactant.

42. **(a)** $p_0=500\,\text{atm}$

$$K=\frac{2.303}{t}\log_{10}\frac{p_0}{p_t}$$

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

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

$\Rightarrow$ $\frac{500}{1.02}=490\,\text{atm}$

43. **(c)** For following reaction,

$$2NO_{(g)}+O_2(g)\longrightarrow 2NO_2(g)$$

When the volume of vessel change into $\frac{1}{3}$ then concentration of reactant become three times.

The rate of reaction for first order reaction $\propto$ concentration.

So rate of reaction will increases three times.

44. **(b)** Let the rate of reaction depends on x^{th} power of [*A*]. Then $r_1=k[A]^x$ and $r_2=k[2A]^x$

$\therefore$ $\frac{r_1}{r_2}=\frac{[A]^x}{[2A]^x}=\frac{1}{4}=\left(\frac{1}{2}\right)^2$ $(\because r_2=4r_1)$

$\therefore$ x = 2. As the reaction rate does not depend upon the concentration of B. Hence, the correct rate law will be rate $=K[A]^2[B]^o$ or $=K[A]^2$

45. **(c)** $k=\frac{2.303}{t}\log_{10}\frac{a}{a-x}$;

$t=2\times 10^2,\ a=800,\ a-x=50$

$$k=\frac{2.303}{2\times 10^2}\log_{10}\frac{800}{50}=\frac{2.303}{2\times 10^2}\log_{10}16\oplus$$

$$=\frac{2.303}{2\times 10^2}\log_{10}2^4=\frac{2.303}{2\times 10^4}\times 4\times 0.301$$

$$=1.38\times 10^{-2}\ s^{-1}$$

46. **(a)** We know that for first order kinetics

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

$(a-x)=0.05\ \text{mol}\ l^{-1}, 6=\frac{2.303}{t}\log\frac{0.5}{0.05}$

or $t=\frac{2.303}{6}\log\frac{0.5}{0.05}=\frac{2.303}{6}=0.384\,\text{min}$

47. **(d)** For $2A+B\longrightarrow C$

Rate $=K[A][B]$

Value of rate constant $K=Ae^{-Ea/RT}$ here *K* is independent of the initial concentration of A and B.

48. **(a)** The concentration of reactant does not change with time for zero order reaction (unit of K suggests zero order) since reactant is in excess.

49. **(b)** $k=\frac{2.303}{t}\log\frac{a}{a-x}$

$$\frac{0.693}{T}=\frac{2.303}{t}\log\frac{100}{100-30}$$

$\therefore$ T = 58.2 min.

50. **(a)** As doubling the initial conc. doubles the rate of reaction, order = 1.

51. **(c)** It is a second order reaction and the unit of *k* for second order reaction is litre $\text{mol}^{-1}\ \text{sec}^{-1}$.

52. **(a)** Rate law for the reaction

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

is $r=k[N_2O_5]$ first order reaction.

53. **(b)** The rate of zero order reaction is not depend on the concentration of the reactants.

54. **(a)** It is a standard example of first order because in that reaction rate of reaction affected by only one concentration term.

55. **(c)** For 1st order reaction

$$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

56. **(b)** The overall order of a reaction is sum of powers T raised on concentration terms in order to write rate expression.

57. **(c)** $k = \frac{0.693}{30} = 0.0231$; $t = \frac{2.303}{k}\log\left(\frac{100}{100-75}\right)$

$$t = \frac{2.303}{0.0231}\log 4 = 60\,\text{minutes}$$

58. **(c)** K for 1st order reaction = per unit time *i.e.* Time^{-1}.

59. **(c)** Rate of zero order reaction is independent of the concentration of the reactant and remains constant throughout the reaction.

60. **(d)** Unit of K for Ist order reaction is Time^{-1}.

NCERT Exemplar Problems

More than One Answer

61. **(a, b)** The reaction is first order with respect to A, The rate of this reaction at 40 sec. will be equal to 3.5×10^{-3} M/sec.

62. **(a, c)** The average energy of the two colliding molecules is less than some minimum amount of energy required for the reaction, Molecules that are improperly oriented during collision will not react.

63. **(b, c)** $\frac{dx}{dt} = K[Zn]^1[H^+]^2$

Rate is not effected if concentration of zinc is made four times and that of H^+ion is halved,

64. **(a,b)** $t = \frac{1}{2k_1}\ln 3$, $t = \frac{1}{2k_2}\ln 3$

65. **(b, d)** Rate constant K is equal to collision frequency A_1 if Ea = 0, Log K Vs $\frac{1}{T}$ is a straight line

66. **(b, c)** increase of temperature of the reaction, increase of concentration of the reactants

67. **(a, b)** Bimolecular reaction, II order reaction

68. **(d)** Catalyst reduces the activation energy for reaction and thus increase the rate of reaction.

69. **(c)** $K = 1.7\times10^{-5}\,s^{-1}$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.7}\times10^5 = 11.3h$$

70. **(a)** Arrhenius equation is $\log k = \log A - \frac{E_a}{RT}$

71. **(b)** In photochemical reaction the rate of formation of product is directly proportional to the intensity of absorbed light.

Assertion and Reason

72. **(a)** For a first order reaction, $K = \frac{2.303}{t}\log\frac{a}{a-x}$, where a is initial concentration, and x is the amount reacted in time t. For half-life x = a/2, t = $t_{1/2}$

$$K = \frac{2.303}{K}\log\frac{a}{a-a/2}$$

$$t_{1/2} = \frac{2.303}{K}\log 2 = \frac{0.693}{K}.$$

73. **(d)** $H_2 + Cl_2 \rightarrow 2HCl$ has much higher quantum efficiency than $H_2 + Br_2 \rightarrow 2HBr$. The first step of secondary process of $H_2 + Cl_2 \rightarrow 2HCl$ is exothermic while the same for $H_2 + Br_2 \rightarrow 2HBr$ is endothermic.

74. **(e)** Vision is a fast photochemical reaction in which the compound, retinal, present in the eye undergoes isomerisation by absorbing a photon of light.

75. **(a)** The emission of cold light during a chemical reaction is called chemiluminescence.

76. **(d)** The rate reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

77. **(a)** Rate expression $\frac{dx}{dt} = K[A]^m[B]^n$ Shows that the total order of reactions is m + n + O = m + n as the rate of reaction is independent of concentration of C, *i.e.* the order with respect to C is zero. This is the reason that C does not figure in the rate expression.

78. **(b)** Instantaneous rate of a reaction is equal to small change in concentration (dx) during a small interval of time (dt) at that particular instent of time divided by the time interval.

79. **(b)** Molecularity of a reaction can be defined only for an elementary reaction because complex reaction does not take place in one single step and it is almost impossible for all the total molecules of the reactants to be in a state of encounter simultaneously.

80. **(b)** For a zero order reaction

$t_{1/2} = [A_0]/2K.$

81. **(b)** According to Arrhenius equation, $K = Ae^{-E_a/RT}$ when $E_a = 0, K = A.$

Comprehension Based

82. **(a)** $k_f = Ae^{-E_f/RT}; k_b = Ae^{-E_b/RT}$

$$\therefore \quad k = \frac{k_f}{k_b} = \frac{Ae^{-E_f/RT}}{Ae^{-E_b/RT}} = e(E_b - E_f)RT$$

$$\log k = \frac{E_b - E_f}{2.303RT}$$

$$= \frac{33000\,J\,mol^{-1}}{2.303 \times 8.314 JK^{-1}mol^{-1} \times 300K} = 5.745$$

$$\therefore \quad k = \text{Antilog}\,(5.745) = 5.55 \times 10^5$$

83. **(b)** $\frac{E_f}{E_b} = \frac{20}{31}$ (given).

$E_f - E_b = -33$ (given) . . .(*i*)

Substituting $E_b = \frac{31}{20}E_f$, in equation (*i*)

we get $E_f - \frac{31}{20}E_f = -33$

$$\frac{-11}{20}E_f = -33$$

$$E_f = \frac{33 \times 20}{11} = 60\text{kJ mol}^{-1}$$

$$E_b = E_f + 33 = 60 + 33 = 93\text{kJ mol}^{-1}$$

84. **(c)** Threshold energy $= E_b + \text{PE of product}$

$= 93 + 30 = 123$ kJ mol^{-1}

85. **(b)** At 2°C(275), the reaction is three times slower than at 27°C (300K).This implies that for souring of milk.

$$\frac{k_{300}}{k_{275}} = 3, T_1 = 275K, T_2 = 300K$$

Applying Arrhenius equation

$$\log\frac{k_{300}}{k_{275}} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_2T_1}\right)$$

$$\log 3 = \frac{E_a}{2.303 \times 8.314}\left(\frac{300 - 275}{275 \times 300}\right)$$

$$E_a = 30.146\,\text{kJ}\,\text{mol}^{-1}$$

86. **(b)** Now $T_1 = 300K, T_2 = 37°C = 310K$

$E_a = 30146\,J\,mol^{-1}$

$$\log\frac{k_{310}}{k_{300}} = \frac{30146\,J\,mol^{-1}}{2.303 \times 8.314} \times \frac{310 - 300}{300 \times 310} = 0.1693$$

$$\therefore \quad \frac{k_{310}}{k_{300}} = \text{anti}\log(0.1693) = 1.477$$

Higher the rate constant, faster is the reaction, *i.e.,* lesser is the time taken, hence

$$\frac{t_{310}}{t_{300}} = \frac{k_{300}}{k_{310}} = \frac{1}{1.477}$$

$$\therefore \quad t_{310} = t_{300} \times \frac{1}{1.477}$$

$$= \frac{48}{1.477} = 3.2.5\text{hr}$$

87. **(a)** $\frac{k_{310}}{k_{300}} = 1.477$

$$\therefore \quad k_{310} = 1.477 \times k_{300} = 1.477 \times 1.6 \times 10^5$$

$$= 2.363 \times 10^5$$

88. **(b)** Since C is taken s excess, so its concentration does not change. So it is not taken in rate expression of the reaction.

89. **(d)** Order of reaction = 3

Units of third order reaction

$= [\text{Conc}]^{1-n} = [\text{Conc}]^{1-3}\text{mol}^{-2}\text{L}^2\text{time}^{-1}$

90. **(a)** $r_1 = k[A]^2[B]$ $r_2 = k[2A]^2[3B]$

$$\frac{r_2}{r_1} = 12 \Rightarrow r_2 = 12r_1$$

Match the Column

91. **(a)** A→ 1; B→ 3,4; C→ 2; D→ 3

(A) Inversion of cane sugar is pseudo first order reaction.

(B) Hydrolysis of ester in the presence of acid is first order while in the presence of base is second order reaction.

(C) Photochemical reactions are of zero order.

(D) SN^2 reactions are of second order.

92. **(c)** A→ 1,2; B→ 3; C→ 1,2; D→ 3,4

93. **(a)** A→4; B→1,3; C→2; D→1,3

94. **(a)** A→ 4; B→ 2; C→ 3; D→ 1

(A) Decomposition of H_2O_2 is a first order reaction.

(B) Temperature coefficient is generally 2~3

(C) $\frac{k}{A}$ = Fraction of collisions which are effective

(D) $t_{99.9\%}p = 10\,t_{1/2}$

95. **(b)** A→4; B→2; C→5; D→1

Integer

96. **(5)** $\frac{-d[RX]}{dt} = k_2[RX][OH^-]$ (by SN^2 path way)

k_2 = rate constant of S_N2 reaction

$$\frac{-d[RX]}{dt} = k_2[RX][OH^-] + k_1[RX]$$

$$-\frac{1}{[RX]}\frac{d[RX]}{dt} = k_2[OH^-] + k_1$$

This is the equation of a straight line for

$-\frac{1}{[RX]}\frac{d[RX]}{dt}$ vs $[OH^-]$ plot with slope equal to k_2 and intercept equal to k_1

From question:

$k_2 = 2\times10^3\,mol^{-1}L\,hr^{-1}, k_1 = 1\times10^2\,hr^{-1}$

$[RX] = 1.0M$ and $[OH^-] = 0.1$ M

Hence, $\frac{-d[RX]}{dt} = 2\times10^3\times1\times0.1 + 1\times10^2\times1$

= 300 mol L^{-1} hr^{-1} = 5 mol L^{-1} min^{-1}

97. **(0)** $t_{1/2} \propto \frac{1}{a_0^{n-1}}$;

$$t_{1/2} = k\cdot\frac{1}{a_0^{n-1}}$$

$$\log t_{1/2} = \log k - (n-1)\log a_0$$

$$\tan 45° = -(n-1) = -(0-1)$$

$$\tan 45° = 1$$

$\therefore$ $n = 0$

98. **(4)** $t_{1/2} = \frac{0.0693}{k_1}$

$$t_{93.75} = \frac{2.303}{k_1}\log\frac{100}{100-93.75}$$

$$= \frac{2.303}{k_1}\log\frac{100}{6.25} = \frac{2.303}{k_1}\log 2^4$$

$$= \frac{4\times2.303\times\log 2}{k_1} = \frac{4\times0.693}{k_1} = 4t_{1/2}$$

99. **(2)** $0.4M \text{ of } A \xrightarrow{30\,min} 0.2M \xrightarrow{30\,min} 0.1M\,(\text{for } A)$

$0.4M \text{ of } B \xrightarrow{20\,min} 0.2M \xrightarrow{20\,min} 0.1M \xrightarrow{20\,min} 0.05\,(\text{for } B)$

($\frac{d[B]}{dt}$ will be doubled and hence $t_{1/2}$ will be halved)

$\therefore$ $\frac{[A]}{[B]} = 2$

100. **(4)** Statements (a) and (c) are correct.

So total score is 3 + 1 = 4

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