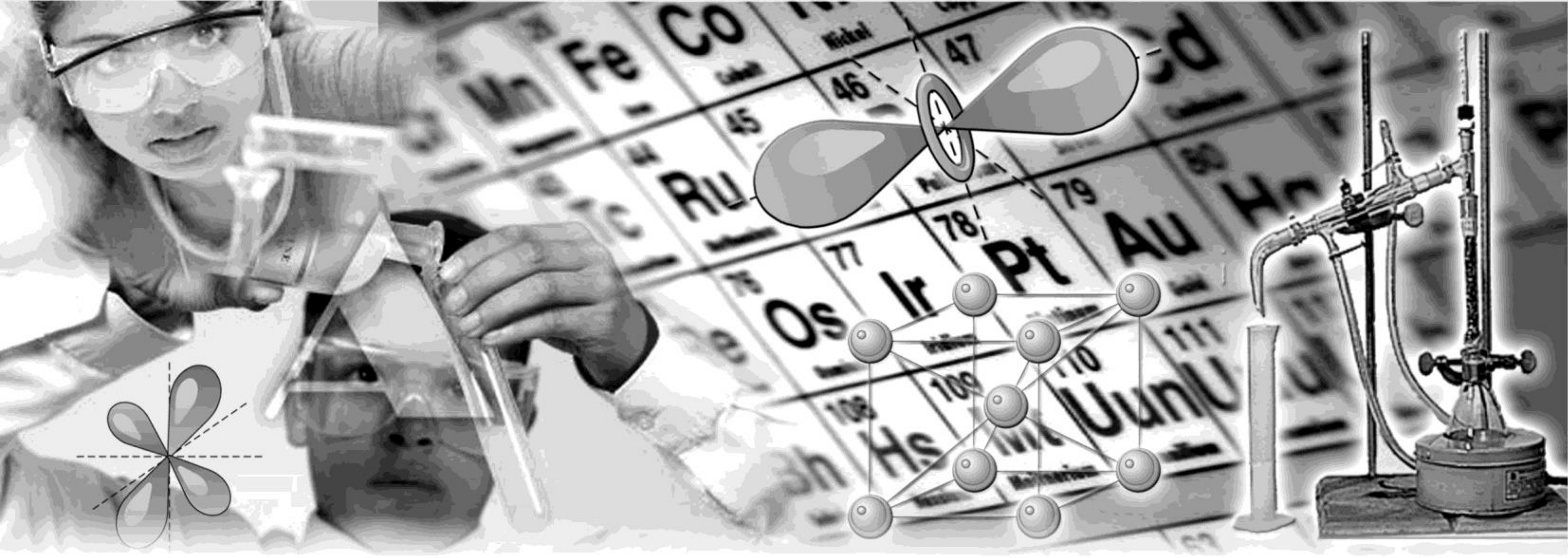


Chapter
11
Chemical Kinetics

The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst etc., on the reaction rates is called the chemical kinetics.

Types of chemical reactions

On the basis of reaction rates, the chemical reactions have been classified into the following three types,

(1) **Very fast or instantaneous reactions :** These reactions occur at a very fast rate generally these reactions involve ionic species and known as ionic reactions. It is almost impossible to determine the rates of these reactions.

Examples

(i) $AgNO_3 + NaCl \rightarrow \underset{\text{(PPt.)}}{AgCl} + NaNO_3$ (*Precipitation reaction*)

(ii) $\underset{\text{(acid)}}{HCl} + \underset{\text{(base)}}{NaOH} \rightarrow \underset{\text{(Salt)}}{NaCl} + H_2O$ (*Neutralization reaction*)

(2) **Moderate reaction :** These reactions proceed with a measurable rates at normal temperature and it is *these reactions are studied in chemical kinetics*. Mostly these reactions are molecular in nature.

Examples

(i) *Decomposition of* H_2O_2 : $2H_2O_2 \rightarrow 2H_2O + O_2$

(ii) *Decomposition of* N_2O_5 : $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

(3) **Very slow reactions :** These reactions are extremely slow and take months together to show any measurable change.

Examples

(i) *Rusting of iron* : $Fe_2O_3 + xH_2O \rightarrow \underset{\text{Hydrated ferricoxide (Rust)}}{Fe_2O_3.xH_2O}$

(ii) $2H_2 + O_2 \xrightarrow{\text{Room temperature}} 2H_2O$

Rate of a reaction

The rate (*speed or velocity*) *of a reaction is the change in concentration in per unit time.*

$$\frac{\Delta x}{\Delta t} \text{ or } \frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1}\right)$$

where Δx or dx is the concentration change, *i.e.,* $(x_2 - x_1)$ in the time interval Δt or dt, *i.e.,* $(t_2 - t_1)$.

Concentration is generally expressed in active mass, *i.e.,* mole L^{-1}

- The rate measured over a long time interval is called *average rate* and the rate measured for an infinitesimally small time interval is called *instantaneous rate* and

Instantaneous rate $= (\text{Average rate})_{\Delta t \rightarrow 0}$

- For the reaction $aA + bB \rightarrow cC + dD$

Rate of disappearance of a reactant is negative

$-\frac{d[A]}{dt}$ = Rate of disappearance of A

$-\frac{d[B]}{dt}$ = Rate of disappearance of B

Rate of formation of a product is positive

$\frac{d[C]}{dt}$ = Rate of formation of C

$\frac{d[D]}{dt}$ = Rate of formation of D

- In terms of stoichiometric coefficient rate may be expressed as

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

- The rate of reaction is always ***positive***.
- The rate of chemical reaction decreases as the reaction proceeds.
- Unit of rate of a reaction = $\frac{\text{Unit of conc.}}{\text{Unit of time}}$ =*mole* L^{-1} *time* $^{-1}$

In term of gaseous reaction the unit is *atm time*$^{-1}$ and

Rate in *atm time*$^{-1}$= Rate in mole $L^{-1} time^{-1} \times RT$

Factors affecting rate of a reaction

The rate of a chemical reaction depends on the following things

(1) **Nature of reactants**

(i) *Physical state of reactants* : This has considerable effect over rate of reaction.

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

(ii) *Physical size of the reactants* : Among the solids, rate increases with decrease in particle size of the solid.

(iii) *Chemical nature of the reactants*

(a) 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.

(b) Oxidation-reduction reactions, which involve transfer of electrons, are also slow as compared to the ionic substance.

(c) Substitution reactions are relatively much slower.

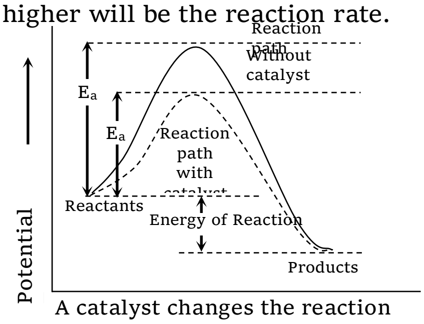
(2) **Effect of temperature :** The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost double or tripled for every 10^oC rise in temperature.

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*.

$$\mu = \text{Temperatur e coefficien t} = \frac{k \text{ at } (t+10^o C)}{k \text{ at } t^o C} = \frac{k_{35^o C}}{k_{25^o C}}$$

(3) **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.

(4) **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.



A catalyst changes the reaction

(5) **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.

Law of mass action and Rate constant

The rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.

- For a reaction, $aA + bB \rightarrow$ product

Rate $= \left(\frac{dx}{dt}\right) \propto [A]^a[B]^b$; $\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$

Where k is called **rate constant** or **velocity constant**.

When $[A]=[B]=1\,mol/litre$, then $\frac{dx}{dt} = k$

Thus, rate constant k is also called **specific reaction rate**.

- The value of rate constant depends on, nature of reactant, temperature and catalyst. It is independent of concentration of the reactants.
- Unit of rate constant $= \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \sec^{-1} = \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \sec^{-1}$

Where $n =$ order of 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 **:** $NH_4NO_2 \rightarrow N_2 + 2H_2O$ *(Unimolecular)*

$NO + O_3 \rightarrow NO_2 + O_2$ *(Bimolecular)*

$2NO + O_2 \rightarrow 2NO_2$ *(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 $xA + yB \rightarrow \text{Products}$

The rate law is $\text{Rate} = [A]^x[B[^y$

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.

$2A + 3B \rightarrow A_2B_3$

$A + B \rightarrow AB\text{(fast)}$

$AB + B_2 \rightarrow AB_3\text{(slow)}$ (*Rate determining step*)

$AB_3 + A \rightarrow A_2B_3\text{(fast)}$

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

- Molecularity of a reaction is derived from the mechanism of the given reaction. Molecularity can not 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***. (Table 11.1)

Table : 11.1 Order and molecularity of some reaction

S. No.	Chemical equation	Molecularity	Rate law	Order w.r.t.		
				First reactant	Second reactant	Overall
1.	$aA + bB \rightarrow$ product	$a + b$	$\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$	a	b	$a + b$
2.	$aA + bB \rightarrow$ product	$a + b$	$\left(\frac{dx}{dt}\right) = k[A]^2[B]^0$	2	zero, if B is in excess	2
3.	$2H_2O_2 \xrightarrow{Pt,\Delta} 2H_2O + O_2$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[H_2O_2]$	1*	-----	1
4.	$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3COOC_2H_5]$	1*	Zero, if H_2O is in excess	1
5.	$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[C_{12}H_{22}O_{11}]$	1*	Zero, if H_2O is in excess	1
6.	$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[(CH_3)_3CCl]$	1*	Zero, if OH^- does not take part in slow step	1
7.	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3Cl][OH^-]$	1	1	2
8.	$C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$	1 (Unimolecular)	$\left(\frac{dx}{dt}\right) = k[C_6H_5N_2Cl]$	1	----	1
9.	$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$	1 (Unimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3CHO]^{3/2}$	1.5	----	1.5
10.	$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	5	$\left(\frac{dx}{dt}\right) = k[H_2O_2][I^-]$	1	1 ($H^+$is medium)	2
11.	$2O_3 \rightarrow 3O_2$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[O_3]^2[O_2]$	1	-1 with respect to O_2	1

*Pseudo-unimolecular reactions.

Table : 11.2 Rate constant and other parameters of different order reactions

Order	Rate constant	Unit of rate constant	Effect on rate by changing conc. to m times	(Half-life period) T_{50}=
0	$k_0 = \frac{x}{t}$	conc. time^{-1} (mol L^{-1} s^{-1})	No change	$\frac{a}{2k_0}$
1	$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$, $C = C_0 e^{-k_1 t}$ $N = N_0 e^{-k_1 t}$, $k_1 = \frac{2.303}{(t_2 - t_1)}\log_{10}\frac{(a-x_1)}{(a-x_2)}$	time^{-1} (s^{-1})	m times	$\frac{0.693}{k_1}$
2	$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{x}{ta(a-x)}$ (for the case when each reactant has equal concentration) $k_2 = \frac{2.303}{t(a-b)}\log_{10}\left[\frac{b(a-x)}{a(b-x)}\right]$(for the case when both reactants have different concentration)	conc^{-1} time^{-1} (mol L^{-1}) s^{-1} L mol^{-1} s^{-1}	m^2 times	$\frac{1}{k_2 a}$
3	$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$	conc^{-2} time^{-1} (mol L^{-1})$^{-2}$ s^{-1} L^2 mol^{-2} s^{-1}	m^3 times	$\frac{3}{2k_3 a^2}$
n	$k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{(a)^{n-1}}\right]$; $n \geq 2$	conc$^{(1-n)}$ time^{-1} (mol L^{-1})$^{(1-n)}$ s^{-1} $L^{(n-1)}$ mol$^{(1-n)}$ s^{-1}	m^n times	$\frac{2^{n-1}-1}{(n-1)k_n(a)^{n-1}}$

Methods for determination of order of a reaction

(1) **Integration method** (Hit and Trial method)

(i) The method can be used with various sets of a, x and t with integrated rate equations.

(ii) The value of k is determined and checked for all sets of a, x and t.

(iii) If the value of k is constant, the used equation gives the order of reaction.

(iv) If all the reactants are at the same molar concentration, the kinetic equations are :

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$ *(For first order reactions)*

$$k = \frac{1}{t}\left[\frac{1}{a} - \frac{1}{a-x}\right]$$ *(For second order reactions)*

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$ *(For third order reactions)*

(2) **Half-life method :** This method is employed only when the rate law involved only one concentration term.

$$t_{1/2} \propto a^{1-n};\ t_{1/2} = ka^{1-n};\ \log t_{1/2} = \log k + (1-n)\log a$$

A plotted graph of $\log t_{1/2}$ *vs log a* gives a straight line with slope $(1-n)$, determining the slope we can find the order n. If half-life at different concentration is given then,

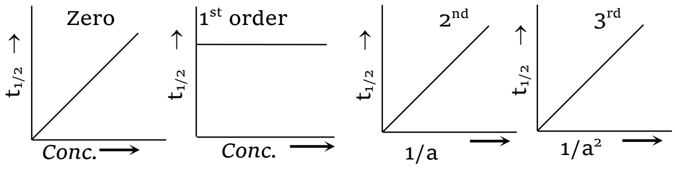
$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}};\ (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}};\ \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)\,[\log_{10} a_2 - \log_{10} a_1]$$

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

This relation can be used to determine order of reaction ‘n’

Plots of half-lives Vs concentrations ($t_{1/2} \propto a^{1-n}$)



(3) **Graphical method :** A graphical method based on the respective rate laws, can also be used.

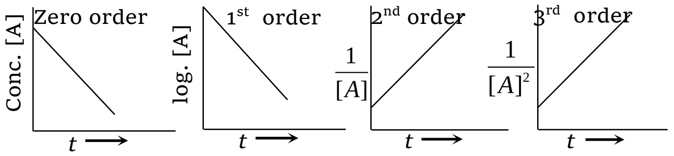
(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\frac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.

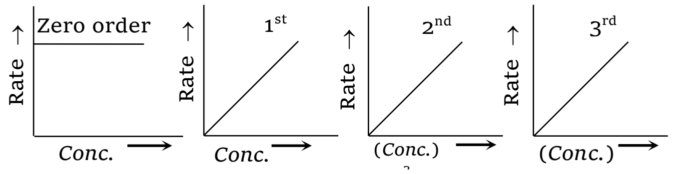
(iii) If the plot of $\frac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

Plots from integrated rate equations



Plots of rate Vs concentrations [Rate = k(conc.)^n]



(4) **Van't Haff differential method :** The rate of reaction varies as the n^{th} power of the concentration Where 'n' is the order of the reaction. Thus for two different initial concentrations C_1 and C_2 equation, can be written in the form,

$$\frac{-dC_1}{dt} = kC_1^n \text{ and } \frac{-dC_2}{dt} = kC_2^n$$

Taking logarithms,

$$\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10} k + n\log_{10} C_1 \quad .....(i)$$

and $$\log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n\log_{10} C_2 \quad .....(ii)$$

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \quad .....(iii)$$

$\frac{-dC_1}{dt}$ and $\frac{-dC_2}{dt}$ are determined from concentration Vs time graphs and the value of 'n' can be determined.

(5) **Ostwald's isolation method** (Initial rate method)

This method can be used irrespective of the number of reactants involved *e.g.,* consider the reaction, $n_1A + n_2B + n_3C \rightarrow \text{Products}$.

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (A, B, C).

Suppose it is observed as follows,

(i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes four times. This means that, Rate $\propto [A]^2$ *i.e.,* order with respect to A is 2

(ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that, Rate $\propto [B]$ *i.e.,* order with respect to B is 1

(iii) Keeping the concentrations of A and B constant, if concentration of C is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of C *i.e.,* order with respect to C is zero. Hence the overall rate law expression will be, Rate = $k[A]^2 [B] [C]^0$

$\therefore$ Overall order of reaction = 2 + 1 + 0 = 3.

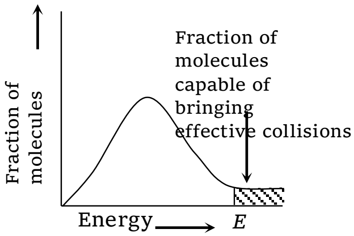
Theories of reaction rate

(1) **Collision theory**

(i) The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of ***collision theory*** for reactions.

(ii) The number of collisions that takes place per second per unit volume of the reaction mixture is known as ***collision frequency*** (Z). The value of collision frequency is very high of the order of 10^{25} to 10^{28} in case of binary collisions.

(iii) Every collision does not bring a chemical change. The collisions that actually produce the product are ***effective collisions***. The effective collisions, which bring chemical change, are few in comparison to the total number of collisions. The collisions that do not form a product are ***ineffective elastic collisions***, *i.e.,* molecules just collide and disperse in different directions with different velocities.



Distribution of energies at a definite temperature

(iv) For a collision to be effective, the following two barriers are to be cleared,

(a) *Energy barrier : "The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy**"*.

- In the graph 'E' corresponds to minimum or threshold energy for effective collision.
- There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy to cross the energy barrier.

(b) *Orientation barrier :* The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed. For example, $NO_2(g) + NO_2(g) \rightarrow N_2O_4(g)$. During this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.

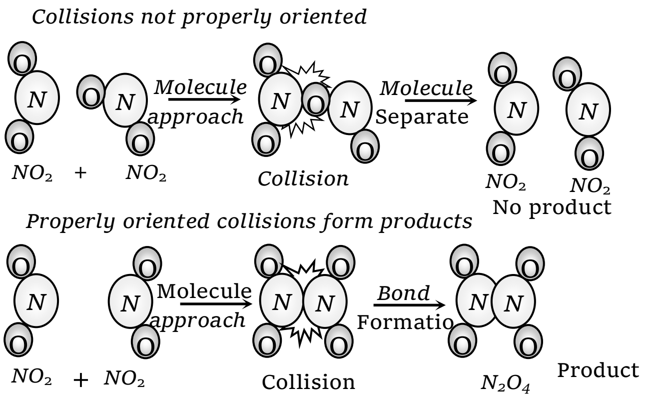


Fig. 11.1

(v) Thus, the main points of ***collision theory*** are as follows,

(a) For a reaction to occur, there must be collisions between the reacting species.

(b) Only a certain fraction of the total number of collisions is effective in forming the products.

(c) For effective collisions, the molecules should possess sufficient energy as well as orientation.

(vi) The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions. Thus, the rate of reaction is proportional to :

(a) The number of collisions per unit volume per second (Collision frequency, Z) between the reacting species

(b) The fraction of effective collisions (Properly oriented and possessing sufficient energy), f *i.e.*,

$$\text{Rate} = \frac{-dx}{dt} = f \times Z$$

Where f is fraction of effective collision and Z is the collision frequency.

(vii) The physical meaning of the activation energy is that it is the minimum relative kinetic energy which the reactant molecules must possess for changing into the products molecules during their collision. This means that the fraction of successful collision is equal to $e^{-E_a/RT}$ called ***Boltzmann factor***.

(viii) It may be noted that besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful. Thus, if Z_{AB} is the collision frequency, P is the ***orientation factor*** (Steric factor) then, $k = PZ_{AB}.e^{-E_a/RT}$. If we compare this equation with Arrhenius equation. $k = Ae^{-E_a/RT}$

We know that pre-exponential form *'A'* in Arrhenius equation is, $A = PZ_{AB}$.

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.

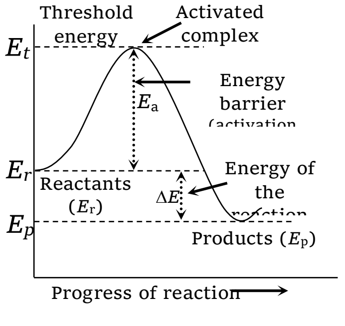
(a) *Zero activation energy* = Fraction of effective collision (f) will be very large = Very fast reaction (Instantaneous reaction).

(b) *Low activation energies* = Fraction of effective collision (f) will be large = Fast reactions.

(c) *High activation energies* = Fraction of effective collision (f) will be small = Slow reaction.

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 absorb 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***.



(2) **Transition state theory**

(i) According to transition state theory the activated complex is supposed to be in equilibrium with the reactant molecules.

(ii) Once the transition state is formed it can either return to the initial reactants or proceeds to form the products.

(iii) 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

(iv) 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

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$$k = A\,e^{-E_a/RT} \qquad .....(i)$$

The equation is called ***Arrhenius equation***.

In which constant A is known as ***frequency factor***. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and

R is the gas constant

Both A and E_a are collectively known as ***Arrhenius parameters***.

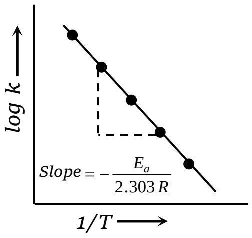
Taking logarithm equation (i) may be written as,

$$\log k = \log A - \frac{E_a}{2.303\,RT} \qquad .....(ii)$$

The value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.

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

Therefore $E_a = -2.303\,R \times \text{slope}$.



Rate constants for the reaction at two different temperatures T_1 and T_2,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad .....(iii)$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively $(T_2 > T_1)$.

Mechanism of the reaction

(1) **Reaction involving first order consecutive reactions**

(i) In such reactions, the reactions form a stable intermediate compound before they are finally converted into the products.

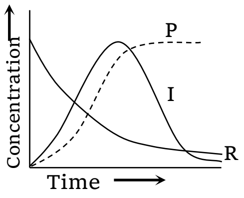
(ii) For example, reactants (R) are first converted to intermediate (I) which is then converted to product (P) as

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

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.



Concentration profile of reactants (R), intermediate (I) and products (P) as a

(2) **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

$R \xrightarrow{k_1} I$; $I \xrightarrow{k_2} P$, if $k_1 << k_2$ then I is converted into products as soon as it is formed, we can say that

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

(3) **Parallel reactions :** In such type of reactions the reactants are more reactive, which may have different orders of the reactions taking place simultaneously. For example, in a system containing

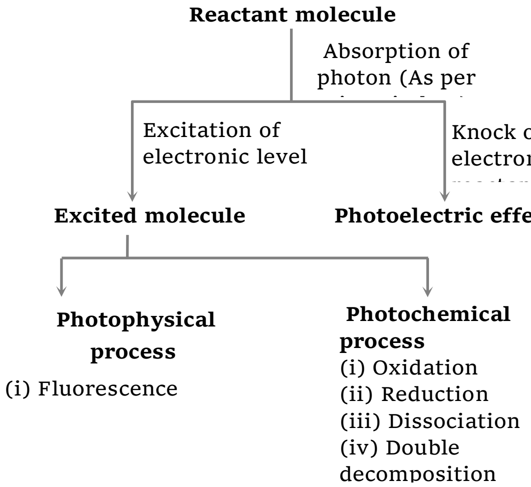
NO_2 and SO_2, NO_2 is consumed in the following two reactions, $2NO_2 \xrightarrow{k_1} N_2O_4$; $NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$

The rate of disappearance of NO_2 will be sum of the rates of the two reactions *i.e.*,

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 + k_2[NO_2][SO_2]$$

Photochemical reaction

Absorption of radiant energy by reactant molecules brings in photophysical 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.

(1) **Characteristics of photochemical reactions**

(i) Each molecule taking part in a photo process absorbs only one photon of radiant energy thereby increasing its energy level by $h\nu \; or \; \frac{hc}{\lambda}$

(ii) Photochemical reactions do not occur in ***dark***.

(iii) 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)

(iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.

(v) The ΔG values for light initiated reactions may or may not be ***negative***.

(vi) The temperature does not have marked effect on the rate of light initiated reactions.

(2) **Mechanism of some photochemical reactions**

(i) ***Photochemical combination of H₂ and Cl₂*** : 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.

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

The mechanism leading to very high yield of *HCl* as a result of chemical change can be as follows. Chlorine molecules absorb radiant energy to form an excited molecule which decomposes to chlorine free radicals (*Cl*) to give chain initiation step.

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

Chain initiation step : $Cl_2^* \rightarrow Cl^\bullet + Cl^\bullet$ ....(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 : $Cl^\bullet + H_2 \rightarrow HCl + H^\bullet$ ....(iii)

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

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

Chain terminating step : $Cl^\bullet + Cl^\bullet \rightarrow Cl_2$ ....(iv)

(ii) ***Photochemical combination of H₂ and Br₂*** : The combination of H_2 and Br_2 to form *HBr* in presence of light is also an example of chain reaction like photochemical combination of H_2 and Cl_2. Here two Br_2 molecules absorb photon, however, inspite of chain reaction only one molecule of *HBr* is formed for each 100 photon absorbed by 100 molecules of Br_2.

$$H_2 + Br_2 \xrightarrow{light} 2HBr$$

Mechanism

Light absorption step : $Br_2 + h\nu \rightarrow Br_2^*$ ....(i)

Chain initiation step : $Br_2^* \rightarrow Br^\bullet + Br^\bullet$ ....(ii)

Chain propagation step : $Br^* + H_2 \rightarrow HBr + H^\bullet$ ....(iii)

$H^* + Br_2 \rightarrow HBr + Br^\bullet$ ....(iv)

Chain termination step : $Br^\bullet + Br^\bullet \rightarrow Br_2$ ....(v)

The lower values of *HBr* formation per photon of light absorbed has been attributed to the fact that step (III) is highly endothermic and thus before step (III) can take place most of the bromine free radicals recombine as per step (V) to give Br_2 molecule and thus providing less feasibility for step (IV) *i.e.* steps regenerating free radicals. Also the decomposition of *HBr* increases with increase in temperature.

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

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

(4) **Application of photochemistry :** Photochemistry has significant role in our daily life. Some of the photochemical reactions commonly known as cited below,

(i) Photosynthesis in plants
(ii) Photography
(iii) The formation and destruction of ozone layer
(iv) Photoetching in electronic industry
(v) Many polymerization reactions.
(vi) Modern printing technology
(vii) Free radical combinations to obtain many compounds.

Tips & Tricks

✍ Different reactions have different rates because their activation energies are different. Lesser the activation energy faster is the reaction.

✍ The reaction, $NO + \frac{1}{2}O_2 \rightarrow NO_2$, exhibits a small negative temperature coefficient and the rate of reaction decreases with increase of temperature.

✍ Fuels in contact with oxygen do not burn by themselves. This is because they need activation energy (provided by the flame) to initiate the reaction. Thus, fuels are thermodynamically unstable (ΔG is –ve) but kinetically stable.

✍ Quantum efficiency of the photochemical reaction, $H_2 + Cl_2 \xrightarrow{hv} 2HCl$ is very high while that of $H_2 + Br_2 \xrightarrow{hv} 2HBr$, is very low. This is because after the chain initiating step $\left(X_2 \xrightarrow{hv} 2X\right)$

$Cl + H_2 \rightarrow HCl + H$ is exothermic whereas

$Br + H_2 \rightarrow HBr + H$ is endothermic.

✍ **Drapper's effect :** $H_2 + Cl_2 \rightarrow 2HCl$, Such reactions are accompanied by the increase in the volume. This is called Drapper's effect. The reason is that the reaction is exothermic and heat released raises the temperature and gas expands resulting in the increase in volume.

✍ **Actinometer :** A device which is used to measure the intensity of radiation is konwn as actimometer. *e.g.,* Uranyl oxalate actinometer.

✍ Amount of the substance left after '*n*' half lives $= \frac{A_0}{2^n}$.

✍ Free energy change (ΔG) for thermochemical reactions is always negative but remember, ΔG for photochemical reaction may not always be negative. It may be +ve also because a part of the light energy absorbed is converted into the free energy of the products.

✍ Negative catalysts or inhibitors are those substances which decrease the rate of a reaction.

✍ Example of fourth order reaction,
$4KClO_3 \rightleftharpoons 3KClO_4 + KCl$

✍ **Grothus-Draper law :** When light falls on a substance, a part of light is absorbed, a part is reflected and a part is transmitted. only that part of light which is absorbed causes a particular reaction to occur.

✍ **Stark's Einstein law of photochemical equivalence** According to this law, every atom or molecule taking part in photochemical reaction absorbs only one quantum of radiaton.

✍ Kinetics of fast reactions can be studied by (i) Relaxation method (ii) Flash photolysis technique etc.

✍ Enzyme catalysed reactions are faster than metal catalysed reactions, the former has lower activation energy.

Ordinary Thinking

Objective Questions

Rate of a reaction

1. The rate of a chemical reaction **[MP PMT 1973; CPMT 1982]**

(a) Increases as the reaction proceeds
(b) Decreases as the reaction proceeds

(c) May increase or decrease during the reaction

(d) Remains constant as the reaction proceeds

2. The rate of a reaction that not involve gases is not dependent on **[CPMT 1988; AFMC 1995]**

(a) Pressure (b) Temperature

(c) Concentration (d) Catalyst

3. The rate at which a substance reacts depends on its

[MP PMT 1987; BHU 1999; KCET 2005]

(a) Atomic weight (b) Equivalent weight

(c) Molecular weight (d) Active mass

4. The rate law for the reaction $RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by Rate $= K_1[RCl]$. The rate of the reaction will be**[IIT 1988]**

(a) Doubled on doubling the concentration of sodium hydroxide

(b) Halved on reducing the concentration of alkyl halide to one half

(c) Decreased on increasing the temperature of the reaction

(d) Unaffected by increasing the temperature of the reaction

5. 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 **[AIIMS 1991]**

(a) Concentration of `A'

(b) Square of concentration of `A'

(c) Under root of the concentration of `A'

(d) Cube of concentration of `A'

6. The rate of chemical reaction at constant temperature is proportional to

(a) The amount of products formed

(b) The product of masses of the reactants

(c) The product of the molar concentration of the reactants

(d) The mean free path of the reaction

7. 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* $dm^{-3}\min^{-1}$

8. When a reaction is progressing

(a) The rate of the reaction goes on increasing

(b) The concentration of the products goes on decreasing

(c) The concentration of the reactants goes on decreasing

(d) The reaction rate always remains constant

Ordinary Thinking

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15. 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}

16. If the concentration of the reactants is increased, the rate of reaction **[MP PMT 1989]**

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

17. Time required for completion of ionic reactions in comparison to molecular reactions is

(a) Maximum (b) Minimum
(c) Equal (d) None

18. For reaction $2A + B \rightarrow$ 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

19. In a reaction $2A + B \rightarrow A_2B$, the reactant A will disappear at **[MP PET 1993]**

(a) Half the rate that B will decrease
(b) The same rate that B will decrease
(c) Twice the rate that B will decrease
(d) The same rate that A_2B will form

20. 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 **[Roorkee 1992]**

(a) 1/10 (b) 1/8
(c) 8 (d) 16

21. A catalyst increases the rate of reaction because it **[EAMCET 1992]**

(a) Increases the activation energy
(b) Decreases the energy barrier for reaction
(c) Decreases the collision diameter
(d) Increases the temperature coefficient

22. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ 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 **[IIT 1994]**

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

23. In the reaction $2A + B \rightarrow A_2B$, if the concentration of A is doubled and of B is halved, then the rate of the reaction will

(a) Increase by four times (b)Decrease by two times
(c) Increase by two times (d) Remain the same

24. The term $\left(-\frac{dc}{dt}\right)$ in a rate equation refers to the **[MP PMT 1996]**

(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

25. The rate of a reaction depends upon the **[Pb. PMT 1999]**

(a) Volume

(b) Force

(c) Pressure

(d) Concentration of reactant

26. For a given reaction $3A + B \rightarrow C + D$ the rate of reaction can be represented by **[DCE 2000]**

(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

27. For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

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) $6\times10^{-4}\,mol\,l^{-1}s^{-1}$

28. 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 **[AFMC 2001]**

(a) $5\times10^{-4}\,mol\ l^{-1}sec^{-1}$ (b) $5\times10^{-5}\,mol\ l^{-1}sec^{-1}$

(c) $6\times10^{-5}\,mol\ l^{-1}\,\mathrm{sec}^{-1}$ (d) $4\times10^{-4}\,mol\,l^{-1}\,\mathrm{sec}^{-1}$

29. The rate of a chemical reaction depends upon **[AFMC 2002]**

(a) Time (b) Pressure

(c) Concentration (d) All of these

30. The rate of disappearance of SO_2 in the reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is $1.28\times10^{-3}\,g/sec$ then the rate of formation of SO_3 is **[JIPMER 2002]**

(a) $0.64\times10^{-3}\,g/sec$ (b) $0.80\times10^{-3}\,g/sec$

(c) $1.28\times10^{-3}\,g/sec$ (d) $1.60\times10^{-3}\,g/sec$

31. When the concentration of A in the reaction $A + B \rightleftharpoons AB$ is doubled, the rate of reaction will be **[MP PMT 2002]**

(a) Doubled (b) Decreased by half

(c) Unchanged (d) Increased by four times

32. The velocity of the chemical reaction doubles every 10^oC rise of temperature. If the temperature is raised by 50^oC, the velocity of the reaction increases to about

(a) 32 times (b) 16 times

(c) 20 times (d) 50 times

33. An increase in temperature by 10^oC, generally increases the rate of a reaction by

(a) 2 times (b) 10 times

(c) 9 times (d) 100 times

34. The temperature coefficient for reaction in which food deteriorates is 2. Then food deteriorates ...... times as rapidly at 25^oC as it does at 5^oC

(a) Two (b) Four

(c) Six (d) Twenty

35. The rate of a reaction is doubled for every 10^o rise in temperature. The increase in reaction rate as a result of temperature rise from 10^o to 100^o is

[KCET 1993; Kerala PET 2002; MP PET 2003]

(a) 112 (b) 512

(c) 400 (d) 614

36. A catalyst increases the rate of a chemical reaction by

[MNR 1988; CPMT 1999; Pb. PMT 2000]

(a) Increasing the activation energy

(b) Decreasing the activation energy

(c) Reacting with reactants

(d) Reacting with products

37. Velocity constant of a reaction at 290 K was found to be 3.2×10^{-3}. At 310 K it will be about **[KCET 1989, 91]**

(a) 1.28×10^{-2} (b) 9.6×10^{-3}

(c) 6.4×10^{-3} (d) 3.2×10^{-4}

38. The temperature coefficient of a reaction is **[MP PMT 2000]**

(a) Specific reaction rate at 25^oC

(b) Rate of the reaction at 100^oC

(c) Ratio of the rate constants at temperatures 35^oC and 25^oC

(d) Ratio of the rate constants at two temperatures differing by 1^oC

39. The main function of a catalyst in speeding up a reaction is

(a) To increase the rate of the forward reaction

(b) To change the reaction path so as to decrease the energy of activation for the reaction

(c) To reduce the temperature at which the reaction can occur

(d) To increase the energy of the molecules of the reactants

40. The rate of a reaction **[CPMT 1973]**

(a) Increases with increase in temperature

(b) Decreases with increase in temperature

(c) Does not depend on temperature

(d) Does not depend on concentration

41. Which of the following statements is false in relation to enzyme **[MP PMT 2003]**

(a) pH affects their functioning

(b) Temperature affects their functioning

(c) They always increase activation energy

(d) Their reactions are specific

42. A reaction is catalysed by 'X'. Here 'X' **[MP PMT 2003]**

(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

43. Which reaction characteristics are changing by the addition of a catalyst to a reaction at constant temperature

(i) Activation energy (ii) Equilibrium constant
(iii) Reaction entropy (iv) Reaction enthalpy **[DCE 2003]**

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

44. The velocity constant of a reaction at 290 K was found to be 3.2×10^{-3}. At 300 K it will be **[MP PMT 2004]**

(a) 1.28×10^{-2} (b) 6.4×10^{-3}
(c) 9.6×10^{-3} (d) 3.2×10^{-4}

45. In which of the following cases, does the reaction go farthest to completion

(a) $K=10^3$ (b) $K=10^{-2}$
(c) $K=10$ (d) $K=1$

46. Rate of reaction **[Pb. CET 2004]**

(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

47. For the reaction $2N_2O_{5(g)}\to 4NO_{2(g)}+O_{2(g)}$, if concentration of NO_2 in 100 seconds is increased by $5.2\times10^{-3}m$. Then rate of reaction will be **[Kerala CET 2005]**

(a) $1.3\times10^{-5}ms^{-1}$ (b) $5\times10^{-4}ms^{-1}$
(c) $7.6\times10^{-4}ms^{-1}$ (d) $2\times10^{-3}ms^{-1}$
(e) $2.5\times10^{-5}ms^{-1}$

48. A first order reaction complete its 10% in 20 minutes then time required to complete its 19% is **[Kerala CET 2005]**

(a) 30 minutes (b) 40 minutes
(c) 50 minutes (d) 38 minutes
(e) 45 minutes

Rate law and Rate constant

1. Which of these does not influence the rate of reaction **[KCET 2005]**

(a) Nature of the reactants
(b) Concentration of the reactants
(c) Temperature of the reaction
(d) Molecularity of the reaction

2. 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 $=K\frac{[C][D]^2}{[A][B]^2}$

3. In the reaction $2N_2O_5\to4NO_2+O_2$, initial pressure is $500\,atm$ and rate constant K is $3.38\times10^{-5}\sec^{-1}$. After 10 minutes the final pressure of N_2O_5 is **[Orissa JEE 2005]**

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

4. The rate law for the reaction

Sucrose + Water $\xrightarrow{[H^+]}$ Glucose + Fructose is given by

(a) Rate $=K$ [sucrose] [water]
(b) Rate $=K$ [sucrose] $[\text{water}]^0$
(c) Rate $=K$ $[\text{sucrose}]^0$ [water]
(d) Rate $=K$ $[\text{sucrose}]^{1/2}$ $[\text{water}]^{1/2}$

5. $A+2B\to C+D$. If $-\frac{d[A]}{dt}=5\times10^{-4}mol\,l^{-1}s^{-1}$ 1, then $-\frac{d[B]}{dt}$ is **[DPMT 2005]**

(a) $2.5\times10^{-4}mol\,l^{-1}s^{-1}$ (b) $5.0\times10^{-4}mol\,l^{-1}s^{-1}$
(c) $2.5\times10-3mol\,l^{-1}s^{-1}$ (d) $1.0\times10^{-3}mol\,l^{-1}s^{-1}$

6. The data for the reaction $A+B\to C$ is **[CBSE PMT 1994] [UPSEAT 2001]**

Exp.	$[A]_0$	$[B]_0$	Initial rate
(1)	0.012	0.035	0.10
(2)	0.024	0.070	0.80
(3)	0.024	0.035	0.10
(4)	0.012	0.070	0.80

The rate law corresponds to the above data is

(a) Rate $=k[B]^3$ (b) Rate $=k[B]^4$
(c) Rate $=k[A][B]^3$ (d) Rate $=k[A]^2[B]^2$

7. The experimental data for the reaction $2A+B_2\to2AB$ is **[CBSE PMT 1997]**

Exp.	$[A]_0$	$[B]_0$	Rate (mole s^{-1})
(1)	0.50	0.50	1.6×10^{-4}
(2)	0.50	1.00	3.2×10^{-4}
(3)	1.00	1.00	3.2×10^{4}

The rate equation for the above data is

(a) Rate $=k[B_2]$ (b) Rate $=k[B_2]^2$
(c) Rate $=k[A]^2[B]^2$ (d) Rate $=k[A]^2[B]$

8. The reaction $2NO(g)+O_2(g)\rightleftharpoons2NO_2(g)$ 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*

9. For a reaction $2A+B\to$ Products, doubling the initial concentration of both the reactants increases the rate by a factor of 8, and doubling the concentration of B alone doubles the rate. The rate law for the reaction is **[MP PET 2001]**

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

10. For a reactions $A+B\to$ 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 **[MP PET/PMT 1998; MP PMT 2003]**

(a) $\text{rate}=k[A][B]$ (b) $\text{rate}=k[A]^2$
(c) $\text{rate}=k[A]^2[B]^1$ (d) $\text{rate}=k[A]^2[B]^2$

11. Velocity constant K of a reaction is affected by

(a) Change in the concentration of the reactant

(b) Change of temperature
(c) Change in the concentration of the product
(d) None of the above

12. 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 $mole^{-1}\min^{-1}$

13. The rate constant of a reaction depends on **[CPMT 1989; DPMT 2001]**
(a) Temperature (b) Mass
(c) Weight (d) Time

14. In a first order reaction the concentration of reactant decreases from $800\,mol/dm^3$ to $50\,mol/dm^3$ is $2\times10^2\sec$. The rate constant of reaction in $\sec^{-1}$ is **[IIT-JEE (Screening) 2003]**
(a) 2×10^4 (b) 3.45×10^{-5}
(c) 1.386×10^{-2} (d) 2×10^{-4}

15. For a reaction $A\rightarrow B$, the rate of reaction quadrupled when the concentration of A is doubled. The rate expression of the reaction is $r = K(A)^n$. when the value of n is
(a) 1 (b) 0
(c) 3 (d) 2

16. The velocity constant of a reaction is *K*. Which of the following statements is not true regarding *K*
(a) *K* is a constant for a reaction at a given temperature
(b) The value of *K* changes when the temperature changes
(c) *K* is the velocity of the reaction at unit concentrations of the reactant
(d) *K* is a constant for all reactions

17. For the following reaction scheme (homogeneous), the rate constant has units : $A+B\xrightarrow{K}C$ **[MP PET 1999]**
(a) $\sec^{-1} mole$ (b) $\sec^{-1}$
(c) $\sec^{-1} litre\ mole^{-1}$ (d) *sec*

18. Which of the following oxides of nitrogen will be the most stable one **[NCERT 1978]**
(a) $2NO_2(g)\rightleftharpoons N_2(g)+2O_2(g); K = 6.7\times10^{16}\,mol\,l^{-1}$
(b) $2NO(g)\rightleftharpoons N_2(g)+O_2(g); K = 2.2\times10^{30}\,mol\,l^{-1}$
(c) $2N_2O_5(g)\rightleftharpoons 2N_2(g)+5O_2(g); K = 1.2\times10^{34}\,mol\,l^{-5}$
(d) $2N_2O(g)\rightleftharpoons 2N_2(g)+O_2(g); K = 3.5\times10^{33}\,mol\,litre^{-1}$

19. The rate of reaction is determined by slow step reaction. The step is called
(a) Reaction rate (b) Activation step
(c) Rate determining step (d) None of the above

20. The rate of the reaction $CCl_3CHO+NO\rightarrow CHCl_3+NO+CO$ is given by Rate $=K[CCl_3CHO][NO]$. If concentration is expressed in moles/litre, the units of *K* are **[MP PET 1993]**
(a) $litre^2\,mole^{-2}\sec^{-1}$ (b) $mole\ litre^{-1}\sec^{-1}$
(c) $litre\,mole^{-1}\sec^{-1}$ (d) $\sec^{-1}$

21. Rate constant for a reaction $H_2+I_2\rightarrow 2HI$ is 49, then rate constant for reaction $2HI\rightarrow H_2+I_2$ is **[Bihar MEE**
(a) 7 (b) 1/49
(c) 49 (d) 21
(e) 63

22. The reaction
$$N_2O_5\,(\text{in } CCl_4 \text{ solution})\rightarrow 2NO_2(\text{solution})+\frac{1}{2}O_2(g)$$
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 $[N_2O_5]=1.25\,mole\,l^{-1}$ **[AFMC 1998]**
(a) $7.75\times10^{-1}mole\,l^{-1}s^{-1}$ (b) $6.35\times10^{-3}mole\,l^{-1}s^{-1}$
(c) $5.15\times10^{-5}mole\,l^{-1}s^{-1}$ (d) $3.85\times10^{-1}mole\,l^{-1}s^{-1}$

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 $[A]=0.5\,mol\,l^{-1}$, when would $[A]$ reach the value 0.05$mol\ l^{-1}$ **[KCET 2000]**
(a) 0.384 *min* (b) 0.15 *min*
(c) 3 *min* (d) 3.84 *min*

24. The rate constant for the reaction, $2N_2O_5\rightarrow 4NO_2+O_2$ is $3\times10^{-5}\sec^{-1}$. If the rate is $2.40\times10^{-5}\,mol\ litre^{-1}\sec^{-1}$. Then the concentration of N_2O_5 (in *mol litre*$^{-1}$) is **[IIT Screening 2000]**
(a) 1.4 (b) 1.2
(c) 0.04 (d) 0.8

25. For the reaction $2N_2O_5\rightarrow 4NO_2+O_2$ rate of reaction and rate constant are 1.02×10^{-4} and $3.4\times10^{-5}\sec^{-1}$ respectively. The concentration of N_2O_5 at that time will be **[BHU 2001]**
(a) 1.732 (b) 3
(c) 1.02×10^{-4} (d) 3.4×10^5

26. The rate law of the reaction $2N_2O_5\rightarrow 4NO_2+O_2$ is **[MP PET 2002]**
(a) $r=K[N_2O_5]$ (b) $r=K[N_2O_5]^2$
(c) $r=K[N_2O_5]^0$ (d) $r=K[NO_2]^4[O_2]$

27. If $R=K[NO]^2[O_2]$, rate constant may be increased by **[BHU 2003]**
(a) Increasing temperature
(b) Decreasing temperature
(c) Increasing concentration of O_2
(d) Increasing concentration of NO

28. The value of rate constant $A+B\rightarrow$ products depends on **[BHU 2003]**
(a) Concentration of *A* and *B*

(b) Pressure
(c) Temperature
(d) All of these

29. The rate constant of a reaction depends upon **[BHU 2004]**
(a) Extent of reaction
(b) Time of reaction
(c) Temperature of the system
(d) Concentration of the system

30. The rate equation for the reaction $2A+B\rightarrow C$ is found to be: rate $=k[A][B]$. The correct statement in relation to this reaction is that the **[AIEEE 2004]**
(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

31. The specific rate constant of a first order reaction depends on the
[IIT 1981, 83; DPMT 1991; Bihar MEE 1995; KCET 1998]
(a) Concentration of the reactants
(b) Concentration of the products
(c) Time of reaction
(d) Temperature of reaction

32. If the concentration is expressed in moles per litre, the unit of the rate constant for a first order reaction is
[MNR 1986; MP PET 1994, 2000, 01;Bihar MEE 1996; CPMT 1997; MP PMT 1995, 96, 99;AFMC 2002]
(a) *mole litre* $^{-1}\sec^{-1}$ (b) *mole litre* $^{-1}$
(c) $\sec^{-1}$ (d) mole $^{-1}$ *litre* $^{-1}$ *sec* $^{-1}$

33. The dimension of rate constant of a second order reaction involves **[NCERT 1982]**
(a) Neither time nor concentration
(b) Only time
(c) Time and concentration
(d) Time and square of concentration

34. The unit of rate constant of second order reaction is usually expressed as
[NCERT 1983, 84; MNR 1983; MP PMT 1994, 99]
(a) *mole litre* $\sec^{-1}$ (b) $mole^{-1}\,litre^{-1}\sec^{-1}$
(c) $mole\ litre^{-1}\sec^{-1}$ (d) $mole^{-1}\,litre\sec^{-1}$

35. A zero order reaction is one whose rate is independent of
[NCERT 1981]
(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

36. The unit of rate constant for a zero order reaction is
[NCERT 1981; MP PMT 2000; RPET 2000]
(a) *litre* $\sec^{-1}$ (b) *litre* *mole* $^{-1}\sec^{-1}$
(c) *mole* $litre^{-1}\sec^{-1}$ (d) *mole* $\sec^{-1}$

37. Which of the following rate laws has an overall order of 0.5 for reaction involving substances x, y and z
[AIIMS 1983]
(a) Rate $=K(C_x)(C_y)(C_z)$
(b) Rate $=K(C_x)^{0.5}(C_y)^{0.5}(C_z)^{0.5}$
(c) Rate $=K(C_x)^{1.5}(C_y)^{-1}(C_z)^{0}$
(d) Rate $=K(C_x)(C_z)^n/(C_y)^2$

38. 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 **[NCERT 1978]**
(a) Zero order (b) First order
(c) Second order (d) Third order

39. For a chemical reaction $A\rightarrow B$ it is found that the rate of reaction doubles, when the concentration of A is increased four times. The order in A for this reaction is
[NCERT 1979; AIIMS 1997; J & K CET 2005]
(a) Two (b) One
(c) Half (d) Zero

40. The following data are for the decomposition of ammonium nitrate in aqueous solution

Volume of N_2 in cc	Time (minutes)
6.25	10
9.50	15
11.42	20
13.65	25
35.05	Finally

The order of the reaction is
(a) Zero (b) One
(c) Two (d) Three

41. The hydrolysis of ethyl acetate is a reaction of
[MP PMT 1987]

$$CH_3COOEt+H_2O\xrightarrow{H^+}CH_3COOH+EtOH$$

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

42. The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds. The order of reaction with respect to A is
[CPMT 1985]
(a) 10 (b) 1
(c) 4 (d) 2

43. Which of the following is a first order reaction
[MP PMT 1987]
(a) $NH_4NO_2\rightarrow N_2+2H_2O$
(b) $2HI\rightarrow H_2+I_2$
(c) $2NO_2\rightarrow 2NO+O_2$
(d) $2NO+O_2\rightarrow 2NO_2$

44. The inversion of cane sugar is represented by
$C_{12}H_{22}O_{11}+H_2O\rightarrow C_6H_{12}O_6+C_6H_{12}O_6$
It is a reaction of
[AFMC 1982; MP PMT 1993; RPET 2000]
(a) Second order (b) Unimolecular
(c) Pseudo unimolecular (d) None of the three

45. Which one of the following formula represents a first order reaction **[MP PMT 1999]**

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

46. The first order rate constant for the decomposition of N_2O_5 is $6.2 \times 10^{-4}\ \sec^{-1}$. The half life period for this decomposition in seconds is **[MNR 1991; MP PET 1997; UPSEAT 2000]**

(a) 1117.7
(b) 111.7
(c) 223.4
(d) 160.9

47. A first order reaction which is 30% complete in 30 minutes has a half-life period of **[AIIMS 1998]**

(a) 24.2 *min*
(b) 58.2 *min*
(c) 102.2 *min*
(d) 120.2 *min*

48. The order of a reaction which has the rate expression $\frac{dc}{dt} = K[E]^{3/2}[D]^{3/2}$ is

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

49. The reaction $2N_2O_5 \rightleftharpoons 2NO_2 + O_2$ follows first order kinetics. Hence, the molecularity of the reaction is

(a) Unimolecular
(b) Pseudo-unimolecular
(c) Bimolecular
(d) None of the above

50. A reaction involving two different reactants **[KCET 1989; AIEEE 2005]**

(a) Can never be a second order reaction
(b) Can never be a unimolecular reaction
(c) Can never be a bimolecular reaction
(d) Can never be a first order reaction

51. 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

52. Catalyst decomposition of hydrogen peroxide is a .... order reaction

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

53. The half life of a first order reaction is

(a) Independent of the initial concentration of the reactant
(b) Directly proportional to the initial concentration of the reactants
(c) Inversely proportional to the initial concentration of the reactant
(d) Directly proportional to the square of the initial concentration of the reactant

54. The decomposition of N_2O_5 is a first order reaction represented by $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$. After 15 *minutes* the volume of O_2 produced is $9\,ml$ and at the end of the reaction $35\,ml$. The rate constant is equal to **[MP PET 1995]**

(a) $\frac{1}{15}\ln\frac{35}{44}$
(b) $\frac{1}{15}\ln\frac{44}{26}$
(c) $\frac{1}{15}\ln\frac{44}{35}$
(d) $\frac{1}{15}\ln\frac{35}{26}$

55. The unit of specific reaction rate constant for a first order (if the concentration expressed in molarity) would be **[MNR 1988; UPSEAT 2000, 01]**

(a) *mole* $litre^{-1}s^{-1}$
(b) *mole* $litre^{-1}$
(c) *mole* s^{-1}
(d) s^{-1}

56. 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

57. Inversion of canesugar in dilute acid (conversion into glucose and fructose) is a

(a) Unimolecular reaction
(b) Bimolecular reaction
(c) Trimolecular reaction
(d) Pseudo-unimolecular reaction

58. The half life period of a first order reaction **[AMU 2000]**

(a) $\frac{0.693}{t}$
(b) $\frac{0.693}{K}$
(c) $\frac{2.303}{t}$
(d) $\frac{0.303}{K_1}$

59. The order of a reaction is said to be 2 with respect to a reactant *X*, when **[DPMT 2000]**

(a) The rate of the reaction is proportional to $[X]$
(b) The rate of the reaction is proportional $[X]^2$
(c) Two molecules of *X* are present in the stoichiometric equation
(d) The reaction occurs in two steps

60. Decay constant of a reaction is $1.1 \times 10^{-9}/\sec$, then the half life of the reaction is

(a) 1.2×10^8
(b) 6.3×10^8
(c) 3.3×10^8
(d) 2.1×10^8

61. If the half life period of a reaction is inversely proportional to the initial concentration, the order of the reaction is

(a) Zero
(b) One
(c) Two
(d) Three

62. Which one of the following statements is wrong

(a) Molecularity of a reaction is always a whole number
(b) Order and molecularity of a reaction need not be same
(c) Order of a reaction may be zero
(d) Order of a reaction depends upon the mechanism of the reaction

63. 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

64. For reation, $A+B \rightarrow$ products, it is found that the rate of the reaction is proportional to the concentration of *A*, but it is independent of the concentration of B, then

(a) The order of the reaction 2 and molecularity 1
(b) Molecularity of the reaction is 2 but order is 1
(c) Order is 2 and molecularity is 2
(d) Order of the reaction is 2 but molecularity is 0

65. 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

66. If '*a*' is the initial concentration and '*n*' is the order of the reaction and the half life period is '*T*', then

[MH CET 2000]

(a) $T \propto a^{n-1}$ (b) $T \propto a^{n}$
(c) $T \propto \frac{1}{a^{n}}$ (d) $T \propto \frac{1}{a^{n-1}}$

67. In presence of HCl, sucrose gets hydrolysed into glucose and fructose. The concentration of sucrose was found to reduce form 0.4 *M* to 0.2 *M* in 1 hour and 0.1 *M* in 2 hours. The order of the reaction is

(a) Zero (b) One
(c) Two (d) None of these

68. The time of half change of a first order reaction in .... initial concentration

(a) Proportional to
(b) Inversely proportional to
(c) Independent of
(d) Equal to

69. Half life period of a first order reaction is 138.6 minutes. The velocity constant of the reaction is

(a) 0.05 min^{-1} (b) 0.00005 min^{-1}
(c) 0.005 min^{-1} (d) 200 min^{-1}

70. An example of a pseudo –unimolecular reaction is

(a) Dissociation of hydrogen iodide
(b) Hydrolysis of methyl acetate in dilute solution
(c) Dissociation of phosphorus pentachloride
(d) Decomposition of hydrogen peroxide

71. About half life period of a first order reaction, which one of the following statements is generally false

(a) It is independent of initial concentration
(b) It is independent of temperature
(c) It decreases with the introduction of a catalyst
(d) It increases with increase of temperature

72. Decomposition of nitrogen pentoxide is known to be a first order reaction 75 percent of the oxide had decomposed in the first 24 minutes. At the end of an hour, after the start of the reaction, the amount of oxide left will be

(a) Nil (b) About 1%
(c) About 2% (d) About 3%

73. A reaction $2A \rightarrow$ products is found to follow zero oder kinetics, then

(a) $\frac{dx}{dt} = k[A]^2$ (b) $\frac{dx}{dt} = k[A]^0$
(c) $\frac{dx}{dt} = k[A]$ (d) $\frac{dx}{dt} = k[2A]$

74. The alkaline hydrolysis of ethyl acetate is represented by the equation

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Experimentally it is found that for this reaction

$\frac{dx}{dt} = k[CH_3COOC_2H_5][NaOH]$

Then the reaction is **[JIPMER 1999]**

(a) Bimolecular and of first order
(b) Bimolecular and of second order
(c) Pseudo–bimolecular
(d) Pseudo–unimolecular

75. For the reaction $2HI \rightleftharpoons H_2 + I_2$, the rate of the reaction is proportional to $[HI]^2$. This means that the reaction is

[AMU 1985; MP PET 2000]

(a) Unimolecular (b) Bimolecular
(c) Of first order (d) Of second order

76. Inversion of sucrose is **[AMU 1988; MP PET 2000]**

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

77. The one which is unimolecular reaction is

[MP PMT 1999; UPSEAT 2001]

(a) $2HI \rightarrow H_2 + I_2$ (b) $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$
(c) $H_2 + Cl_2 \rightarrow 2HCl$ (d) $PCl_3 + Cl_2 \rightarrow PCl_5$

78. Integrated velocity equation for first order reaction is

(a) $[A]_o = [A]e^{-Kt}$ (b) $K = [A]_o e^{-A/t}$
(c) $Kt = 2.303 \log \frac{[A]_o}{[A]}$ (d) $\log \frac{[A]_o}{[A]} = -2.303\, Kt$

79. If the surface area of the reactants increases, then order of the reaction

(a) Increases
(b) Decreases
(c) Remain constant
(d) Sometimes increases and sometimes dereases

80. Half life period $t_{1/2}$ for first order reaction is

(a) K (b) $\frac{1.303 \log 2}{K}$
(c) $\frac{2.303 \log 2}{K}$ (d) $\frac{9}{K}$

81. Molecularity of reaction of inversion of sugar is

(a) 3 (b) 2

(c) 1 (d) 0

82. For any reaction, if we plot a graph between time '*t*' and $\log(a-x)$, a simple line is obtained. The order of reaction is

(a) Zero (b) One

(c) Two (d) Three

83. Value of velocity constant for first order reaction is $3.46\times10^{-3}\ \text{min}^{-1}$, the time for half change is

(a) 100 minutes (b) 400 minutes

(c) 200 minutes (d) 346 minutes

84. The unit of the velocity constant in case of zero order reaction is **[CPMT 1994]**

(a) $Conc.\times time^{-1}$ (b) $Conc.^{-1}\times time$

(c) $Conc.^{-1}\times time^{-1}$ (d) $Conc.\times(time)^2$

85. For the reaction $H_2(g)+Br_2(g)\rightarrow 2HBr(g)$, the experimental data suggest, rate $=K[H_2][Br_2]^{1/2}$. The molecularity and order of the reaction are respectively

[CPMT 1988; MP PET 1993]

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

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

86. The incorrect order indicated against the rate of reaction $A+B\xrightarrow{K}C$ is **[BHU 1990]**

Rate	Order
(a) $\frac{d[C]}{dt}=K[A]$	1
(b) $\frac{d[C]}{dt}=K[A][B]$	2
(c) $\frac{-d[A]}{dt}=K[A][B]^0$	2
(d) $\frac{-d[A]}{dt}K[A]$	1

87. Which of the following statements regarding the molecularity of a reaction is wrong **[CBSE PMT 1989]**

(a) It is the number of molecules of the reactants taking part in a single step chemical reaction

(b) It is calculated from the reaction mechanism

(c) It may be either a whole number or fractional

(d) It depends on the rate determining step in the reaction

88. Diazonium salt decomposes as

$C_6H_5N_2^+Cl^-\rightarrow C_6H_5Cl+N_2$

At 0^oC, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is **[MNR 1994; UPSEAT 2002]**

(a) A first order reaction

(b) A second order reaction

(c) Independent of the initial concentration of the salt

(d) A zero order reaction

89. In the reaction $A+B\rightarrow$ Products, if B is taken in excess, then it is an example of **[EAMCET 1992]**

(a) Second order reaction

(b) Zero order reaction

(c) Pseudounimolecular reaction

(d) First order reaction

90. The half life of a first order reaction is $69.35\ \text{sec}$. The value of the rate constant of the reaction is **[CBSE PMT**

(a) $1.0\,s^{-1}$ (b) $0.1\,s^{-1}$

(c) $0.01\,s^{-1}$ (d) $0.001\,s^{-1}$

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

[KCET 1992]

(a) $1.25\,g$ (b) $0.63\,g$

(c) $1.77\,g$ (d) $0.5\,g$

92. The half life of a first order reaction is 10 minutes. If initial amount is $0.08\,mol/litre$ and concentration at some instant is $0.01\,mol/litre$, then $t=$ **[Roorkee 1990]**

(a) 10 minutes (b) 30 minutes

(c) 20 minutes (d) 40 minutes

93. Half life period of second order reaction is **[MP PMT 1994]**

(a) Proportional to the initial concentration of reactants

(b) Independent of the initial concentration of reactants

(c) Inversely proportional to initial concentration of reactants

(d) Inversely proportional to square of initial concentration of reactants

94. The reaction $2H_2O_2\rightarrow 2H_2O+O_2$ is a

[Manipal MEE 1995]

(a) Zero order reaction (b) First order reaction

(c) Second order reaction (d)Third order reaction

95. In a reaction involving hydrolysis of an organic chloride in presence of large excess of water

$RCl+H_2O\rightarrow ROH+HCl$ **[MP PET 1995]**

(a) Molecularity is 2, order of reaction is also 2

(b) Molecularity is 2, order of reaction is 1

(c) Molecularity is 1, order of reaction is 2

(d) Molecularity is 1, order of reaction is also 1

96. The thermal decomposition of a compound is of first order. If a sample of the compound decomposes 50% in 120 minutes, in what time will it undergo 90% decomposition

[MP PET 1996]

(a) Nearly 240 *minutes* (b) Nearly 480 *minutes*

(c) Nearly 450 *minutes* (d) Nearly 400 *minutes*

97. The order of a reaction with rate equals $kC_A^{3/2}C_B^{-1/2}$ is

[MP PET 1996, 2001]

(a) 2 (b) 1

(c) $-\frac{1}{2}$ (d) $\frac{3}{2}$

98. If the rate expression for a chemical reaction is given by Rate $=k[A]^m[B]^n$ **[MP PMT 1996]**

(a) The order of the reaction is m

(b) The order of the reaction is n

(c) The order of the reaction is $m+n$

(d) The order of the reaction is $m-n$

99. The half-life period of a first order reaction is 100 *sec*. The rate constant of the reaction is **[MP PMT 1997; MP PET 2001]**

(a) $6.93\times10^{-3}\ \text{sec}^{-1}$ (b) $6.93\times10^{-4}\ \text{sec}^{-1}$

(c) $0.693\ \text{sec}^{-1}$ (d) $69.3\ \text{sec}^{-1}$

100. For the first order reaction with rate constant k, which expression gives the half-life period ? (Initial concentration $=a$) **[MP PET/PMT 1998]**

(a) $\frac{1^2}{k}$ (b) $\frac{1}{ka}$

(c) $\frac{0.693}{k}$ (d) $\frac{3}{2ka^2}$

101. The rate constant of a first order reaction whose half-life is 480 seconds, is **[MP PET 1999]**

(a) $2.88\times10^{-3}\ \text{sec}^{-1}$ (b) $1.44\times10^{-3}\ \text{sec}^{-1}$

(c) $1.44\ \text{sec}^{-1}$ (d) $0.72\times10^{-3}\ \text{sec}^{-1}$

102. The conversion of $A\rightarrow B$ follows second order kinetics. Doubling the concentration of A will increase the rate of formation of B by a factor **[MP PET 1999; DCE 1999; KCET 2001; BCECE 2005]**

(a) $1/4$ (b) 2

(c) $1/2$ (d) 4

103. The reaction $2FeCl_3+SnCl_2\rightarrow2FeCl_2+SnCl_4$ is an example of **[CBSE PMT 1996; MP PET 1999]**

(a) First order reaction

(b) Second order reaction

(c) Third order reaction

(d) None of these

104. If reaction between A and B to give C shows first order kinetics in A and second order in B, the rate equation can be written as **[MP PET 1999]**

(a) Rate $=k[A][B]^{1/2}$ (b) Rate $=k[A]^{1/2}[B]$

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

105. For a first order reaction, the half-life period is independent of **[CBSE PMT 1999]**

(a) Initial concentration

(b) Cube root of initial concentration

(c) First power of final concentration

(d) Square root of final concentration

106. Order of a reaction can have **[DPMT 1996]**

(a) $+ve$ values (b) Whole number values

(c) Fractional values (d) All of the above

107. The order of the reaction occurring by following mechanism should be **[JIPMER 1997]**

(i) $A_2\rightarrow A+A$ (fast)

(ii) $A+B_2\rightarrow AB+B$ (slow)

(iii) $A+B\rightarrow$ (fast)

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

(c) 2 (d) None of these

108. For the reaction $A\rightarrow B$, the rate law expression is : Rate $=k[A]$

Which of the following statements is incorrect **[Pb. PMT 1998]**

(a) The reaction is said to follow first order kinetics

(b) The half life of the reaction will depend on the initial concentration of the reactant

(c) k is constant for the reaction at a constant temperature

(d) The rate law provides a simple way of predicting the concentration of reactants and products at any time after the start of the reaction

109. If initial concentration is reduced to its 1/4th in a zero order reaction, the time taken for half of the reaction to complete **[BHU 1998]**

(a) Remains same (b) Becomes 4 times

(c) Becomes one-fourth (d) Doubles

110. For a reaction whose rate expression is :

Rate $=k[A]^{1/2}[B]^{3/2}$, the order would be **[Pune CET 1998]**

(a) 1.5 (b) 2

(c) 3 (d) 1

111. For the reaction $A\rightarrow B$, the rate increases by a factor of 2.25 when the concentration of A is increased by 1.5. What is the order of the reaction **[KCET 1**

(a) 3 (b) 0

(c) 2 (d) 1

112. For the reaction $H_2+Cl_2\xrightarrow{\text{Sunlight}}2HCl$ taking place on water, the order of reaction is **[KCET 1998; AIIMS 2002; Pb. PMT 2002]**

(a) 1 (b) 2

(c) 3 (d) 0

113. For a first order reaction, rate constant is $0.6932\ hr^{-1}$, then half-life for the reaction is **[Bihar MEE 199**

(a) $0.01\,hr$ (b) $1\,hr$

(c) $2\,hr$ (d) $10\,hr$

(e) $0.1\,hr$

114. The rate constant of a reaction is $0.69\times10^{-1}\ \text{min}^{-1}$ and the initial concentration is $0.2\,mol\,l^{-1}$. The half-life period is **[AIIMS 1998]**

(a) 400 *sec* (b) 600 *sec*

(c) 800 *sec* (d) 1200 *sec*

115. The rate constant of a first order reaction is 3×10^{-6} per second. If the initial concentration is 0.10 *m*, the initial rate of reaction is **[AFMC 1999 Pb. PMT 1999, 2000; BHU 1999; AIIMS 1999; KCET 2000; DCE 2004]**

(a) $3\times10^{-5}ms^{-1}$ (b) $3\times10^{-6}ms^{-1}$

(c) $3\times10^{-8}ms^{-1}$ (d) $3\times10^{-7}ms^{-1}$

116. Certain bimolecular reactions which follow the first order kinetics are called

(a) First order reactions

(b) Unimolecular reactions

(c) Bimolecular reactions

(d) Pseudounimolecular reactions

117. The rate law of the reaction $A + 2B \rightarrow$ Product is given by $\frac{d[dB]}{dt} = k[B^2]$. If A is taken in excess, the order of the reaction will be **[AMU (Engg.) 1999]**

(a) 1

(b) 2

(c) 3

(d) 0

118. For a first order reaction $A \rightarrow$ product, the rate of reaction at $[A] = 0.2\ mol\ l^{-1}$ is $1.0 \times 10^{-2} mol\ l^{-1}\ \min^{-1}$. The half life period for the reaction is **[Roorkee 1999]**

(a) 832 *s*

(b) 440 *s*

(c) 416 *s*

(d) 13.86 *s*

119. For the reaction $A + B \rightarrow$ products, doubling the concentration of *A* the rate of the reaction is doubled, but on doubling the concentration of *B* rate remains unaltered. The over all order of the reaction is **[JIPMER 1999]**

(a) 1

(b) 0

(c) 2

(d) 3

120. Which among the following is a false statement **[KCET 1999]**

(a) Half life of a third order reaction is inversely proportional to the square of initial concentration of the reactant.

(b) Molecularity of a reaction may be zero or fractional

(c) For a first order reaction $t_{1/2} = \frac{0.693}{K}$

(d) Rate of zero order reaction is independent of initial concentration of reactant

121. After how many seconds will the concentration of the reactants in a first order reaction be halved, if the decay constant is $1.155 \times 10^{-3}\ \sec^{-1}$ **[CBSE PMT 2000]**

(a) 100 *sec*

(b) 200 *sec*

(c) 400 *sec*

(d) 600 *sec*

122. What is the order of a reaction which has a rate expression rate $= K[A]^{3/2}[B]^{-1}$ **[DCE 2000]**

(a) 3/2

(b) 1/2

(c) 0

(d) None of these

123. Which of the following expression is correct for first order reaction? (*CO*) refers to initial concentration of reactant **[DCE 2000]**

(a) $t_{1/2} \propto CO$

(b) $t_{1/2} \propto CO^{-1}$

(c) $t_{1/2} \propto CO^{-2}$

(d) $t_{1/2} \propto CO^{0}$

124. For a reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$. When concentration of Cl_2 is doubled, the rate of reaction becomes two times of the original. When the concentration of *NO* is doubled the rate becomes four times. What is the order of the reaction **[MP PMT 2000]**

(a) 1

(b) 2

(c) 3 **[KCET (Med.) 1999]**

(d) 4

125. The rate constant for a second order reaction is $8 \times 10^{-5} M^{-1} min^{-1}$. How long will it take a 1*M* solution to be reduced to 0.5 *M* **[MH CET 2001]**

(a) 8×10^{-5} *min*

(b) 8.665×10^{3} *min*

(c) 4×10^{-5} *min*

(d) 1.25×10^{4} *min*

126. The rate for a first order reaction is $0.6932 \times 10^{-2} mol\ l^{-1} min^{-1}$ and the initial concentration of the reactants is 1*M*, $T_{1/2}$ is equal to **[JIPMER (Med.) 2001]**

(a) 6.932 *min*

(b) 100 *min*

(c) 0.6932×10^{-3} *min*

(d) 0.6932×10^{-2} *min*

127. For a given reaction $t_{1/2} = \frac{1}{Ka}$.. The order of the reaction is **[KCET 2001]**

(a) 1

(b) 0

(c) 3

(d) 2

128. 75% of a first order reaction is completed in 30 minutes. What is the time required for 93.75% of the reaction (in minutes) **[KCET 2001]**

(a) 45

(b) 120

(c) 90

(d) 60

129. A First order reaction is half completed in 45 minutes. How long does it need 99.9% of the reaction to be completed **[AIIMS 2001]**

(a) 5 hours

(b) 7.5 hours

(c) 10 hours

(d) 20 hours

130. A substance '*A*' decomposes by a first order reaction starting initially with [A] =2.00m and after 200 min [A] = 0.15m. For this reaction what is the value of *k* **[AIIMS 2001]**

(a) $1.29 \times 10^{-2}\ \min^{-1}$

(b) $2.29 \times 10^{-2}\ \min^{-1}$

(c) $3.29 \times 10^{-2}\ \min^{-1}$

(d) $4.40 \times 10^{-2}\ \min^{-1}$

131. Which of the following statements about zero order reaction is not true

(a) Its unit is sec^{-1}

(b) The graph between log (reactant) versus rate of reaction is a straight line

(c) The rate of reaction increases with the decrease in concentration of reactants

(d) Rate of reaction is independent of concentration of reactants

132. The given reaction $2NO + O_2 \rightarrow 2NO_2$ is an example of **[CBSE PMT 2001; JIPMER 2002]**

(a) First order reaction

(b) Second order reaction

(c) Third order reaction

(d) None of these

133. Order of a reaction is decided by **[KCET 2002]**

(a) Pressure

(b) Temperature

(c) Molecularity

(d) Relative concentration of reactants

134. From the following which is a second order reaction

[AMU 2002]

(a) $K = 5.47\times10^{-4}\ \text{sec}^{-1}$

(b) $K = 3.9\times10^{-3}\text{mole lit sec}^{-1}$

(c) $K = 3.94\times10^{-4}\text{lit mole}^{-1}\ \text{sec}^{-1}$

(d) $K = 3.98\times10^{-5}\text{lit mole}^{-2}\ \text{sec}^{-1}$

135. For the reaction $A+2B\rightarrow C,$ rate is given by $R = [A][B]^2$ then the order of the reaction is **[AIEEE 2002]**

(a) 3 (b) 6

(c) 5 (d) 7

136. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively **[AIEEE 2002]**

(a) $sec^{-1},\ M\,sec^{-1}$ (b) $sec^{-1},\ M$

(c) $M\,sec^{-1},\ sec^{-1}$ (d) M, sec^{-1}

137. The reaction $2N_2O_5 \rightleftharpoons 2N_2O_4+O_2$ is **[MP PMT 2002]**

(a) Bimolecular and second order

(b) Unimolecular and first order

(c) Bimolecular and first order

(d) Bimolecular and zero order

138. The half-life period for a first order reaction is 693 seconds. The rate constants for this reaction would be

[MP PET 2002]

(a) $0.1 sec^{-1}$ (b) $0.01 sec^{-1}$

(c) $0.001 sec^{-1}$ (d) $0.0001 sec^{-1}$

139. For an elementary reaction, $2A + B\rightarrow C + D$ the molecularity is **[Kurukshetra CEE 2002]**

(a) Zero (b) One

(c) Two (d) Three

140. If the order of the reaction $x+y\xrightarrow{hv}xy$ is zero, it means that the rate of **[Kurukshetra CEE 2002]**

(a) Reaction is independent of temperature

(b) Formation of activated complex is zero

(c) Reaction is independent of the concentration of reacting species

(d) Decomposition of activated complex is zero

141. For a first order reaction velocity constant, $K = 10^{-3} s^{-1}$. Two third life for it would be**[MP PET 2001; UPSEAT 2003]**

(a) 1100 *s* (b) 2200 *s*

(c) 3300 *s* (d) 4400 *s*

142. In a reaction, the concentration of reactant is increased two times and three times then the increases in rate of reaction were four times and nine times respectively, order of reaction is

(a) Zero (b) 1

(c) 2 (d) 3

143. For a chemical reaction....can never be a fraction

[EAMCET 2003]

(a) Order (b) Half-life

(c) Molecularity (d) Rate constant

144. 75% of a first order reaction was completed in 32 minutes when was 50% of the reaction completed

[AMU 1999; Kerala (Med.) 2003]

(a) 16 *min.* (b) 24 *min.*

(c) 8 *min.* (d) 4 *min.*

145. The decomposition of N_2O_5 occurs as, $2N_2O_5\rightarrow 4NO_2+O_2$, and follows Ist order kinetics, hence

[BVP 2003]

(a) The reaction is unimolecular

(b) The reaction is bimolecular

(c) $T_{1/2}\propto a^0$

(d) None of these

146. Which equation is correct for first order reactions

[MP PMT 2003]

(a) $t_{1/2}\propto C^{-1}$ (b) $t_{1/2}\propto C$

(c) $t_{1/2}\propto C^0$ (d) $t_{1/2}\propto C^{1/2}$

147. For the reaction system $2NO(g)+O_2(g)\rightarrow 2NO_2(g)$ volume is suddenly produced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will **[AIEEE 2003]**

(a) Diminish to one fourth of its initial value

(b) Diminish to one eighth of its initial value

(c) Increase to eight times of its initial value

(d) Increase to four times of its initial value

148. If the rate of the reaction is equal to the rate constant, the order of the reaction is **[CBSE PMT 2003]**

(a) 3 (b) 0

(c) 1 (d) 2

149. The reaction $A\rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of *A* to produce 0.6 mole of *B* is 1 *hour*. What is the time taken for conversion of 0.9 mole of *A* to produce 0.675 mole of *B* **[CBSE PMT 2003]**

(a) 2 *hours* (b) 1 *hour*

(c) 0.5 *hour* (d) 0.25 *hour*

150. The unit of velocity constant in case of zero order reaction is

[MP PMT 2004]

(a) $\text{Concentration}\times\text{Time}^{-1}$ (b) $\text{Concentration}^{-1}\times\text{Time}^{-1}$

(c) $\text{Concentration}\times\text{Time}^{2}$ (d) $\text{Concentration}^{-1}\times\text{Time}$

151. Which one of the following is wrongly matched

[KCET 2004]

(a) Saponification of $CH_3COOC_2H_5$ – Second order reaction

(b) Hydrolysis of CH_3COOCH_3 – Pseudo uni-molecular

[UPSEAT 2003]

reaction

(c) Decomposition of H_2O_2 – First order reaction

(d) Combination of H_2 and Br_2 to give HBr – Zero order

reaction

152. Which of the following is an example of pseudo unimolecular reaction **[Pb. CET 2001]**

(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) $2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$

(d) $NaOH + HCl \rightarrow NaCl + H_2O$

153. Hydrolysis of DDT is a first order reaction, its half life is 10 years. Time to hydrolyse 10 *g* DDT to half is **[BVP 2004]**

(a) 100 years (b) 50 years

(c) 5 years (d) 10 years

154. 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 **[AIEEE 2004]**

(a) 7.5 minutes (b) 15 minutes

(c) 30 minutes (d) 60 minutes

155. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is **[DCE 2004]**

(a) 2 *hr* (b) 4 *hr*

(c) 1/2 *hr* (d) 1/4 *hr*

156. For a reaction, $X(g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. In What period of time would the concentration of *X* be reduced to 10% of original concentration **[DCE 2004]**

(a) 20 *min* (b) 33 *min*

(c) 15 *min* (d) 25 *min*

157. A first order reaction with respect to the reactant *A* has a rate constant of $6\ \sec^{-1}$. If we start with [*A*] = 0.5 mol/litre, then in what time the concentration of *A* becomes 0.05 mol/litre **[DCE 2004]**

(a) 0.384 *sec* (b) 0.214 *sec*

(c) 3.84 *sec* (d) 0.402 *sec*

158. Order of radioactive disintegration reaction is **[JEE Orissa 2004]**

(a) Zero (b) First

(c) Second (d) Third

159. The rate of a first order reaction is $1.5 \times 10^{-2}\ molL^{-1}\ \min^{-1}$ at 0.5 *M* concentration of the reactant. The half life of the reaction is **[CBSE PMT 2004]**

(a) 8.73 *min* (b) 7.53 *min*

(c) 0.383 *min* (d) 23.1 *min*

160. A first order reaction was started with a decimolar solution of the reactant, 8 minutes and 20 seconds later its concentration was found to be $M/100$. So the rate of the reaction is **[Kerala PMT 2004]**

(a) $2.303 \times 10^{-5}\ \sec^{-1}$ (b) $2.303 \times 10^{-4}\ \sec^{-1}$

(c) $4.606 \times 10^{-3}\ \sec^{-1}$ (d) $2.606 \times 10^{-5}\ \sec^{-1}$

(e) $2.603 \times 10^{-4}\ \sec^{-1}$

161. Which is correct about zero order reaction **[JEE Orissa 2004]**

(a) Rate of reaction depends on decay constant

(b) Rate of reaction is independent of concentration

(c) Unit of rate constant is concentration^{-1}

(d) Unit of rate constant is concentration^{-1} time^{-1}

162. Decay of ${}_{92}U^{235}$ is .....order reaction **[JEE Orissa 2004]**

(a) Zero (b) First

(c) Second (d) Third

163. The half-life of 2 sample are 0.1 and 0.4 seconds. Their respective concentration are 200 and 50 respectively. What is the order of the reaction **[JEE Oriss**

(a) 0 (b) 2

(c) 1 (d) 4

164. The following statements(s) is(are) correct **[IIT 1999]**

(a) A plot of $\log K_p$ *versus* $1/T$ is linear

(b) A plot of $\log[X]$ *versus* time is linear for a first order reaction $X \rightarrow P$

(c) A plot of $\log P$ *versus* $1/T$ is linear at constant volume

(d) A plot of P *versus* $1/V$ is linear at constant temperature

165. For a first order reaction **[IIT 1998]**

(a) The degree of dissociation is equal to $(1 - e^{-kt})$

(b) A plot of reciprocal concentration of the reactant *vs* time gives a straight line

(c) The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction

(d) The pre-exponential factor in the Arrhenius equation has the dimension of time T^{-1}

166. For reaction a $A \rightarrow x\ P$, when $[A] = 2.2\ mM$, the rate was found to be $2.4\ mM\ s^{-1}$. On reducing concentration of *A* to half, the rate changes to $0.6\ mM\ s^{-1}$. The order of reaction with respect to *A* is **[AIIMS 2005]**

(a) 1.5 (b) 2.0

(c) 2.5 (d) 3.0

167. Which one of the following statement for order of reaction is not correct **[IIT 2005]**

(a) Order can be determined experimentally.

(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.

(c) It is not affected with the stoichiometric coefficient of the reactants.

(d) Order cannot be fractional.

168. $t_{\frac{1}{4}}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is K, the $t_{\frac{1}{4}}$ can be written as **[AIEEE 2005]**

(a) $0.10 / K$ (b) $0.29 / K$

(c) $0.69 / K$ (d) $0.75 / K$

169. For a first order reaction $A \rightarrow B$ the reaction rate at reactant concentration of $0.01M$ is found to be $2.0 \times 10^{-5} mol\ L^{-1} s^{1}$. The half life period of the reaction is **[CBSE PMT 2005]**

(a) 220 *s* (b) 30 *s*

(c) 300 *s* (d) 347 *s*

170. 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

171. If a substance with half life 3 days is taken at other place in 12 days. What amount of substance is left now **[AFMC 2005]**

(a) 1/4 (b) 1/8

(c) 1/16 (d) 1/32

172. 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*

173. For the reaction $A + B \rightarrow C$, it is found that doubling the concentration of *A* increases the rate by 4 times, and doubling the concentration of *B* doubles the reaction rate. What is the overal order of the reaction. **[KCET 2005]**

(a) 4 (b) 3/2

(c) 3 (d) 1

174. Which of the following reactions end in finite time

[DPMT 2005]

(a) 0 order (b) 1st order

(c) 2nd order (d) 3rd order

Collision theory, Energy of activation and Arrhenius equation

1. A large increase in the rate of a reaction for a rise in temperature is due to **[EAMCET 1980; MP PET 1995]**

(a) The decrease in the number of collisions

(b) The increase in the number of activated molecules

(c) The shortening of the mean free path

(d) The lowering of the activation energy

2. Which of the following statements is not true according to collision theory of reaction rates

(a) Collision of molecules is a precondition for any reaction to occur

(b) All collisions result in the formation of the products

(c) Only activated collisions result in the formation of the products

(d) Molecules which have acquired the energy of activation can collide effectively

3. According to the collision theory of chemical reactions

(a) A chemical reaction occurs with every molecular collision

(b) Rate is directly proportional to the number of collisions per second

(c) Reactions in the gas phase are always of zero order

(d) Reaction rates are of the order of molecular speeds

4. According to the collision theory of reaction rates, rate of reaction increases with temperature due to

[CBSE PMT 2005]

(a) Greater number of collisions

(b) Greater velocity of the reacting molecules

(c) Greater number of molecules have activation energy

(d) None of the above

5. The reaction rate at a given temperature becomes slower, then

[MP PMT 1993; DPMT 2000]

(a) The free energy of activation is higher

[BHU 2005]

(b) The free energy of activation is lower

(c) The entropy changes

(d) The initial concentration of the reactants remains constant

6. A rise in temperature increases the velocity of a reaction. It is because it results in

(a) An increased number of molecular collisions

(b) An increased momentum of colliding molecules

(c) An increase in the activation energy

(d) A decrease in the activation energy

7. The number of collisions depend upon

(a) Pressure (b) Concentration

(c) Temperature (d) All the above

8. If E_f and E_r are the activation energies of forward and reverse reactions and the reaction is known to be exothermic, then

(a) $E_f > E_r$

(b) $E_f < E_r$

(c) $E_f = E_r$

(d) No relation can be given between E_f and E_r as data are not sufficient

9. According to Arrhenius theory, the activation energy is

(a) The energy it should possess so that it can enter into an effective collision

(b) The energy which the molecule should possess in order to undergo reaction

(c) The energy it has to acquire further so that it can enter into a effective collison

(d) The energy gained by the molecules on colliding with another molecule

10. The energy of activation is

(a) The energy associated with the activated molecules

(b) Threshold energy – energy of normal molecules

(c) Threshold energy + energy of normal molecules

(d) Energy of products – energy of reactants

11. Which one of the following does not represent Arrhenius equation

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

(b) $\log_e k = \log_e A - \frac{E}{RT}$

(c) $\log_{10} k = \log_{10} A - \frac{E}{2.303\,RT}$

(d) $k = AE^{-RT}$

12. On increasing the temperature, the rate of the reaction increases because of

(a) Decrease in the number of collisions
(b) Decrease in the energy of activation
(c) Decrease in the number of activated molecules
(d) Increase in the number of effective collisions

13. Energy of activation of a reactant is reduced by

(a) Increased temperature (b) Reduced temperature
(c) Reduced pressure (d) Increased pressure

14. The minimum energy a molecule should possess in order to enter into a fruitful collision is known as

[Kurukshetra CEE 2002]

(a) Reaction energy (b) Collision energy
(c) Activation energy (d) Threshold energy

15. Activation energy is

(a) The amount of energy to be added to the actual energy of a molecule so that the threshold energy is reached
(b) The amount of energy the molecule must contain so that it reacts
(c) The energy which a molecule should have in order to enter into an effective collision
(d) The average kinetic energy of the molecule

16. The reason for almost doubling the rate of reaction on increasing the temperature of the reaction system by 10^{oC} is

[J & K 2005]

(a) The value of threshold energy increases
(b) Collision frequency increases
(c) The fraction of the molecule having energy equal to threshold energy or more increases
(d) Activation energy decreases

17. The activation energy for a simple chemical reaction $A \to B$ is E_a in forward direction. The activation energy for reverse reaction

(a) Is always double of E_a
(b) Is negative of E_a
(c) Is always less than E_a
(d) Can be less than or more than E_a

18. Arrhenius equation is

(a) $\frac{d \ln K}{dT} = \Delta E^* / RT$ (b) $\frac{d \ln K}{dT} = \Delta E^* / RT^2$
(c) $\frac{d \ln K}{dT} = -\Delta E^* / RT^2$ (d) $\frac{d \ln K}{dT} = -\Delta E^* / RT$

19. Activation energy of any reaction depends on

(a) Temperature
(b) Nature of reactants
(c) Number of collisions per unit time
(d) Concentration of reactants

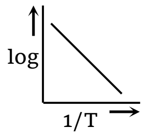
20. Relation between rate constant and temperature by Arrhenius equation is

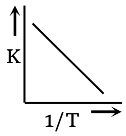
(a) $\log_e A = \log_e K + \frac{E_a}{RT}$ (b) $\log K = A\frac{E_a}{RT}$
(c) $\log_e K = \log_e A - \frac{E_a}{RT^2}$ (d) $\log A = RT \ln E_a - \ln K$

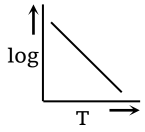
21. An endothermic reaction $A \to B$ has an activation energy $15\,kcal/mole$ and energy of reaction $5\,kcal/mole$. The activation energy of the reaction $B \to A$ is **[Pb. CET 1985]**

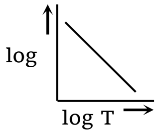
(a) 20 *kcal/mole* **[MP PMT 1997]** (b) 15 *kcal/mole*
(c) 10 *kcal/mole* (d) None of these

22. Which of the following plots is in accordance with the Arrhenius equation

(a) 

(b) 

(c) 

(d) 

23. The Arrhenius equation expressing the effect of temperature on the rate constant of a reaction is**[MP PET**

(a) $k = e^{-E_a/RT}$ (b) $k = E_a / RT$
(c) $k = \log_e \frac{E_a}{RT}$ (d) $k = Ae^{-E_a/RT}$

24. For a reaction, activation energy $(E_a) = 0$ and rate constant $(K) = 3.2 \times 10^6\,s^{-1}$ at 300 *K*. What is the value of the rate constant at 310 *K*

(a) $3.2 \times 10^{-12}\,s^{-1}$ (b) $3.2 \times 10^6\,s^{-1}$
(c) $6.4 \times 10^{12}\,s^{-1}$ (d) $6.4 \times 10^6\,s^{-1}$

25. Activation energy is given by the formula**[DCE 1999]**

(a) $\log \frac{K_2}{K_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

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

(c) $\log \frac{K_1}{K_2} = -\frac{E_a}{2.303\,R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$

(d) None of these

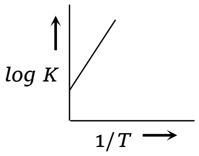
26. A reaction having equal activation energies for forward and reverse reaction has **[CBSE PMT 2003]** **[MP PMT 2002]**

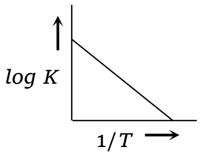
(a) $\Delta H = 0$ (b) $\Delta S = 0$
(c) Zero order (d) None of these

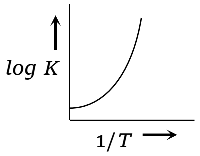
27. Collision theory is applicable to **[MP PMT 2002]**

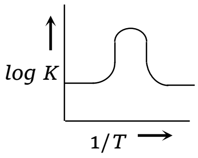
(a) First order reactions (b) Zero order reactions
(c) Bimolecular reactions (d)Intra molecular reactions

28. A graph plotted between log *K* vs 1/*T* for calculating activation energy is shown by **[MP PET 2002]**

(a) 

(b) 

(c) 

(d) 

29. The rate constant of a reaction at temperature 200*K* is 10 times less than the rate constant at 400 *K*. What is the activation energy (E_a) of the reaction (*R* = gas constant)

[EAMCET 2003]

(a) 1842.4 *R* (b) 921.2 *R*

(c) 460.6 *R* (d) 230.3 *R*

30. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statement is correct

[AIEEE 2003]

(a) *k* is equilibrium constant

(b) *A* is adsorption factor

(c) E_a is energy of activation

(d) *R* is Rydberg's constant

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

[JEE Orissa 2004]

(a) 34 (b) 54

(c) 100 (d) 50

32. 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

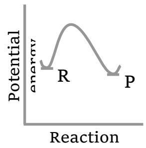
33. The rate constant is given by the equation $k = pze^{-E/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly **[MP PET/PMT 199[illegible]]**

(a) T (b) Z

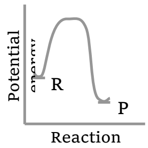
(c) E (d) p

34. An endothermic reaction with high activation energy for the forward reaction is given by the diagram: **[AIIMS 2005]**

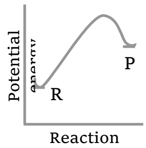
(a)



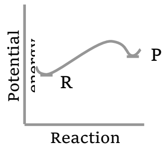
(b)



(c)



(d)



35. Consider an endothermic reaction $X \to Y$ with the activation energies E_b and E_f for the backward and forward reactions, respectively, in general **[AIEEE 2005]**

(a) $E_b < E_f$

(b) $E_b > E_f$

(c) $E_b = E_f$

(d) There is no definite relation between E_b and E_f

36. Temperature dependent equation can be written as

[Orrisa JEE 2005]

(a) $\ln k = \ln A - e^{E_a/RT}$ (b) $\ln k = \ln A + e^{E_a/RT}$

(c) $\ln k = \ln A - e^{RT/E_a}$ (d) All of these

Photochemical reactions

1. The formation of starch in plants results from

(a) Photosynthesis (b) Photolysis

(c) Flash photolysis (d) None of the above

2. The photolysis of water gives the substance

(a) $OH^- + H^+$ (b) $H_2 + OH^-$

(c) $H_2 + O_2$ (d) $H_2O + H_2O_2$

3. The law of photochemical equivalence was given by

(a) Drapper (b) Grauths

(c) Einstein (d) Labbert

4. If *'I'* is the intensity of absorbed light and *C* is the concentration of *AB* for the photochemical process $AB + h\nu \to AB^*$, the rate of formation of *AB** is directly proportional to **[IIT Screening 2001]**

(a) C (b) I

(c) I^2 (d) $C.I$

Critical Thinking

Objective Questions

1. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the rate of reaction is expressed as **[CBSE PMT 1997; AIEEE 2002]**

(a) $-\dfrac{\Delta[I_2]}{\Delta t} = -\dfrac{\Delta[H_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[HI]}{\Delta t}$

(b) $\dfrac{\Delta[I_2]}{\Delta t} = \dfrac{\Delta[H_2]}{\Delta t} = \dfrac{\Delta[HI]}{2\Delta t}$

(c) $\dfrac{\Delta[H_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[I_2]}{\Delta t} = -\dfrac{\Delta[HI]}{\Delta t}$

(d) None of these

2. If $3A \to 2B$, then the rate of reaction of $+\dfrac{d(B)}{dt}$ is equal to

[CBSE PMT 2002]

(a) $+2\dfrac{d(A)}{dt}$ (b) $-\dfrac{1}{3}\dfrac{d(A)}{dt}$

(c) $-\dfrac{2}{3}\dfrac{d(A)}{dt}$ (d) $-\dfrac{3}{2}\dfrac{d(A)}{dt}$

3. The differential rate law for the reaction $H_2 + I_2 \to 2HI$ is **[AIEEE 2002]**

(a) $-\dfrac{d[H_2]}{dt} = -\dfrac{d[I_2]}{dt} = +\dfrac{1}{2}\dfrac{d[HI]}{dt}$

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

(c) $\frac{1}{2}\frac{d[H_2]}{dt}=\frac{1}{2}\frac{d[I_2]}{dt}=-\frac{d[HI]}{dt}$

(d) $-2\frac{d[H_2]}{dt}=-2\frac{d[I_2]}{dt}=+\frac{d[HI]}{dt}$

4. 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) $2^{(n-m)}$

5. If we plot a graph between log K and $\frac{1}{T}$ by Arrhenius equation, the slope is **[UPSEAT 2001]**

(a) $-\frac{E_a}{R}$ (b) $+\frac{E_a}{R}$

(c) $-\frac{E_a}{2.303\,R}$ (d) $+\frac{E_a}{2.303\,R}$

6. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be **[IIT 1992]**

(a) Less than ΔH (b) Zero

(c) More than ΔH (d) Equal to ΔH

7. The rate constant (K') of one reaction is double of the rate constant (K'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions ($E_a^{'}$ and $E_a^{''}$) will be

[MP PET 1994; UPSEAT 2001]

(a) $E_a^{'}>E_a^{''}$ (b) $E_a^{'}=E_a^{''}$

(c) $E_a^{'}<E_a^{''}$ (d) $E_a^{'}=4E_a^{''}$

8. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at $25^\circ C$ are $3.0\times10^{-4}s^{-1}$, $104.4\,kJ\,mol^{-1}$ and $6.0\times10^{14}s^{-1}$ respectively. The value of the rate constant as $T\to\infty$ is

[IIT 1996]

(a) $2.0\times10^{18}s^{-1}$ (b) $6.0\times10^{14}s^{-1}$

(c) Infinity (d) $3.6\times10^{30}s^{-1}$

9. The ΔH value of the reaction $H_2+Cl_2\rightleftharpoons 2HCl$ is $-44.12\,kcal$. If E_1 is the activation energy of the products, then for the above reaction **[EAMCET 1997]**

(a) $E_1>E_2$

(b) $E_1<E_2$

(c) $E_1=E_2$

(d) ΔH is not related to E_1 and E_2

(e) None is correct

10. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $K=A.e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting **[CBSE PMT 2003]**

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

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

11. Activation energy of a chemical reaction can be determined by **[CBSE PMT 1998; AFMC 1999; BHU 2000]**

(a) Changing concentration of reactants

(b) Evaluating rate constant at standard temperature

(c) Evaluating rate constants at two different temperatures

(d) Evaluating velocities of reaction at two different temperatures

[AIEEE 2003]

12. The activation energy for a reaction is $9.0\,K\,cal/mol$. The increase in the rate constant when its temperature is increased from 298K to 308K is **[JIPMER 2000]**

(a) 63% (b) 50%

(c) 100% (d) 10%

13. Which of the following is the fastest reaction

[Pb. CET 2002]

(a) $C+\frac{1}{2}O_2\xrightarrow{250^\circ C}CO$ (b) $C+\frac{1}{2}O_2\xrightarrow{500^\circ C}CO$

(c) $C+\frac{1}{2}O_2\xrightarrow{750^\circ C}CO$ (d) $C+\frac{1}{2}O_2\xrightarrow{1000^\circ C}CO$

14. The rate constant k, for the reaction $N_2O_5(g)\to 2NO_2(g)+\frac{1}{2}0_2(g)$ is $2.3\times10^{-2}s^{-1}$. Which equation given below describes the change of $[N_2O_5]$ with time? $[N_2O_5]_0$ and $[N_2O_5]_t$ correspond to concentration of N_2O_5 initially and at time, t **[AIIMS 2004**

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

(b) $[N_2O_5]_0=[N_2O_5]_te^{kt}$

(c) $\log_{10}[N_2O_5]_t=\log_{10}[N_2O_5]_0-kt$

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

15. For the reaction $CH_3COOCH_3+H_2O\xrightarrow{H^+}CH_3COOH+CH_3OH$ The progress of the process of reaction is followed by

(a) Finding the amount of methanol formed at different intervals

(b) Finding the amount of acetic acid formed at different intervals

(c) Using a voltmeter

(d) Using a polarimeter

16. Half life of a reaction is found to be inversely proportional to the cube of its initial concentration. The order of reaction is

[KCET 2002]

(a) 2 (b) 5

(c) 3 (d) 4

17. The integrated rate equation is $Rt=\log C_0-\log C_t$. The straight line graph is obtained by plotting **[AIEEE 200**

(a) $\text{time v/s }\log C_t$ (b) $\frac{1}{\text{time}}\text{ v/s }C_t$

(c) $\text{time v/s }C_t$ (d) $\frac{1}{\text{time}}\text{ v/s }\frac{1}{C_t}$

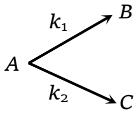
18. For which order reaction a straight line is obtained along with x-axis by plotting a graph between half life $(t_{1/2})$ and initial concentration 'a'

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

19. The reaction, $X \rightarrow$ product follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M Then the rate of reaction when concentration of X is 0.01 M

(a) $1.73 \times 10^{-4} M\ \text{min}^{-1}$ (b) $3.47 \times 10^{-5} M\ \text{min}^{-1}$
(c) $3.47 \times 10^{-4} M\ \text{min}^{-1}$ (d) $1.73 \times 10^{-5} M\ \text{min}^{-1}$

20. A Substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



$k_1 = 1.26 \times 10^{-4} s^{-}$
$k_1 = 3.8 \times 10^{-5} s^{-1}$

The percentage distribution of B and C are

[Kerala PMT 2004]

(a) 75% B and 25% C (b) 80% B and 20% C
(c) 60% B and 40% C (d) 90% B and 10% C
(e) 76.83% B and 23.17% C

AR Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason 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.

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

2. 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.

3. 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.

4. 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.

5. Assertion : According to steady state hypothesis, in a multistep reaction, the change in concentration with time for reactive intermediates is zero.
Reason : The intermediates are so reactive that after a brief initial period their concentrations rise from zero to a small value and remains constant for most of the duration of the reaction.

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

7. Assertion : The photochemical reactions $H_2 + Cl_2 \rightarrow 2HCl$ and $H_2 + Br_2 \rightarrow 2HBr$ have equal quantum efficiencies.
Reason : Both the reactions proceed by similar mechanism.

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

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

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

11. Assertion : The kinetic of the reaction $mA + nB + pC \rightarrow m'X + n'Y + p'Z$ 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.

Answers

Rate of a reaction

1	b	2	a	3	d	4	b	5	b
6	c	7	c	8	c	9	a	10	b
11	b	12	b	13	c	14	d	15	b
16	b	17	c	18	b	19	d	20	a
21	b	22	a	23	d	24	c	25	a
26	a	27	a	28	b	29	b	30	b
31	a	32	c	33	b	34	a	35	c
36	d	37	a	38	b	39	a	40	c
41	a	42	b						

Rate law and Rate constant

1	d	2	c	3	a	4	b	5	a
6	a	7	a	8	c	9	b	10	b
11	b	12	d	13	a	14	c	15	d
16	d	17	c	18	a	19	c	20	c
21	b	22	a	23	a	24	d	25	b
26	a	27	a	28	c	29	c	30	d
31	d	32	c	33	c	34	d	35	b
36	c	37	c	38	a	39	c	40	b
41	a	42	d	43	a	44	c	45	c
46	a	47	b	48	b	49	c	50	b
51	b	52	a	53	a	54	d	55	d
56	c	57	d	58	b	59	b	60	b
61	c	62	d	63	c	64	b	65	c
66	d	67	b	68	c	69	c	70	b
71	d	72	d	73	b	74	b	75	d
76	b	77	b	78	c	79	c	80	c
81	b	82	b	83	c	84	a	85	a
86	c	87	c	88	a	89	c	90	c
91	b	92	b	93	c	94	b	95	b
96	d	97	b	98	c	99	a	100	c
101	b	102	d	103	c	104	c	105	a
106	d	107	a	108	b	109	c	110	b
111	c	112	d	113	b	114	b	115	d
116	d	117	b	118	d	119	a	120	b
121	d	122	b	123	d	124	c	125	d
126	b	127	d	128	d	129	b	130	a
131	ac	132	c	133	d	134	c	135	a
136	a	137	c	138	c	139	d	140	c
141	c	142	c	143	c	144	a	145	c
146	c	147	c	148	b	149	b	150	a
151	d	152	a	153	d	154	c	155	c
156	b	157	a	158	b	159	d	160	c
161	b	162	b	163	b	164	abd	165	ad
166	b	167	d	168	b	169	d	170	b
171	c	172	c	173	c	174	a		

Collision theory, Energy of activation and Arrhenius equation

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

Photochemical reaction

1	a	2	a	3	c	4	b		

Critical Thinking Questions

1	a	2	c	3	a	4	d	5	c
6	c	7	c	8	b	9	a	10	d
11	c	12	a	13	d	14	d	15	b
16	d	17	a	18	b	19	c	20	e

Assertion & Reason

1	b	2	b	3	b	4	b	5	a
6	a	7	d	8	e	9	a	10	d
11	a								

Answers

Rate of a reaction

1	b	2	a	3	d	4	b	5	b
6	c	7	c	8	c	9	a	10	b
11	b	12	b	13	c	14	d	15	b
16	b	17	c	18	b	19	d	20	a
21	b	22	a	23	d	24	c	25	a
26	a	27	a	28	b	29	b	30	b
31	a	32	c	33	b	34	a	35	c
36	d	37	a	38	b	39	a	40	c
41	a	42	b						

Rate law and Rate constant

1	d	2	c	3	a	4	b	5	a
6	a	7	a	8	c	9	b	10	b
11	b	12	d	13	a	14	c	15	d
16	d	17	c	18	a	19	c	20	c
21	b	22	a	23	a	24	d	25	b
26	a	27	a	28	c	29	c	30	d
31	d	32	c	33	c	34	d	35	b
36	c	37	c	38	a	39	c	40	b
41	a	42	d	43	a	44	c	45	c
46	a	47	b	48	b	49	c	50	b
51	b	52	a	53	a	54	d	55	d
56	c	57	d	58	b	59	b	60	b
61	c	62	d	63	c	64	b	65	c
66	d	67	b	68	c	69	c	70	b
71	d	72	d	73	b	74	b	75	d
76	b	77	b	78	c	79	c	80	c
81	b	82	b	83	c	84	a	85	a
86	c	87	c	88	a	89	c	90	c
91	b	92	b	93	c	94	b	95	b
96	d	97	b	98	c	99	a	100	c
101	b	102	d	103	c	104	c	105	a
106	d	107	a	108	b	109	c	110	b
111	c	112	d	113	b	114	b	115	d
116	d	117	b	118	d	119	a	120	b
121	d	122	b	123	d	124	c	125	d
126	b	127	d	128	d	129	b	130	a
131	ac	132	c	133	d	134	c	135	a
136	a	137	c	138	c	139	d	140	c
141	c	142	c	143	c	144	a	145	c
146	c	147	c	148	b	149	b	150	a
151	d	152	a	153	d	154	c	155	c
156	b	157	a	158	b	159	d	160	c
161	b	162	b	163	b	164	abd	165	ad
166	b	167	d	168	b	169	d	170	b
171	c	172	c	173	c	174	a		

Collision theory, Energy of activation and Arrhenius equation

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

Photochemical reaction

1	a	2	a	3	c	4	b		

Critical Thinking Questions

1	a	2	c	3	a	4	d	5	c
6	c	7	c	8	b	9	a	10	d
11	c	12	a	13	d	14	d	15	b
16	d	17	a	18	b	19	c	20	e

Assertion & Reason

1	b	2	b	3	b	4	b	5	a
6	a	7	d	8	e	9	a	10	d
11	a								

AS Answers and Solutions

Rate of a reaction

1. (b) Rate of reaction continuously decreases with time.

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

3. (d) According to law of mass action.

4. (b) $R = K[RCl]$, if $[RCl]$ =1/2, then rate = $R/2$.

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

6. (c) The rate of chemical reaction $\propto$ The product of the molar conc. of the reactants (at constant T)

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

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

8. (c) As reaction progressing the concentration of the reactants decreases and the concentration of the product increases.

9. (a) $\frac{-d(N_2)}{dt} = -\frac{1}{3}\frac{d(H_2)}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt} = \frac{3}{2} \times 40 \times 10^{-3}$

$= 60 \times 10^{-3}$.

10. (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.

11. (b) Ionic reactions are very fast reactions i.e. take place instantaneously.

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

13. (c) 'A' will disappear at twice the rate at which 'B' will decrease.

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

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

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

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

19. (d) The rate of a reaction depends upon concentration of reactant.

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

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

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

$\therefore \frac{\Delta[H_2]}{\Delta t} = \frac{3}{2} \times \frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2} \times 2 \times 10^{-4}$

$= 3 \times 10^{-4}\ mol\ litre^{-1} sec^{-1}$

22. (a) Increase in concentration of $B = 5 \times 10^{-3} mol\ l^{-1}$

$Time = 10$ sec

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

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

24. (c) The rate of formation of SO_3 is $1.28 \times 10^{-3}\ g/sec$.

26. (a) $\frac{K_{t+10}}{K_t} = \frac{r_{t+10}}{r_t} = 2$; For an increase of temperature to 50^oC, *i.e.* 5 times, the rate increases by 2^5 times, *i.e.* 32 times.

28. (b) $\frac{K_{t+10}}{K_t} = \frac{r_{t+10}}{r_t} = 2$.

For an increase of temperature to $20°C$ *i.e.* 2 times, the rate increase by 2^2 times, *i.e.* 4 times.

29. (b) $\frac{k_{t+10}}{K_t} = \frac{r_{t+10}}{r_t} = 2$

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

30. (b) Catalyst increases the rate by decreasing the activation energy.

31. (a) For 10K rise in temperature, the rate of reaction nearly doubles.

32. (c) Temperature coefficient $\frac{K_{35^oC}}{K_{25^oC}} = \frac{K_{308\,k}}{K_{298\,k}} = 2$ and 3 for most reactions.

33. (b) Catalyst decrease energy of activation.

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

35. (c) Enzymes does not always increase activation energy.

36. (d) Catalyst reduce the activation energy for reaction and thus increase the rate of reaction.

37. (a) Catalyst affect only activation energy. It brings down the activation energy of reaction.

38. (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 300 K, velocity constant $=2(K_{290})=2\times3.2\times10^{-3}=6.4\times10^{-3}$.

39. (a) Higher the value of rate constant so, faster the reaction rate.

40. (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.

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

Rate of reaction with respect to NO_2

$$=\frac{1}{4}\frac{d[NO_2]}{dt}=\frac{1}{4}\times\frac{5.2\times10^{-3}}{100}=1.3\times10^{-5}ms^{-1}$$

42. (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 minutes

Rate law and Rate constant

1. (d) Molecularity of the reaction does not influence the rate of reaction.

2. (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.

3. (a) $p_0=500\ atm$

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

$$3.38\times10^{-5}=\frac{2.303}{10\times60}\log\frac{500}{p_t}$$

or $0.00880=\log\frac{500}{p_t}\Rightarrow\frac{500}{1.02}=490\ atm$

4. (b) It is a pseudo-unimolecular reaction.

5. (a) $A+2B\rightarrow C+D$

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

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

8. (c) For following reaction, $2NO_{(g)}+O_2(g)\rightarrow 2NO_2(g)$

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.

9. (b) $2A+B\rightarrow$ Products

According to question : Rate of reaction of 'A' $\propto$ [B] as increase in rate is double when [B] is doubled.

Rate of reaction $\propto$ [A] [B] as increase in rate is 8 times when concentration of both reactant is doubled. It means that order of reaction is 3 and overall rate reaction should be $r=K[A]^2[B]$

10. (b) Let the rate of reaction depends on x^{th} power of [A]. Then

$r_1=k[A]^x$ and $r_2=k[2A]^x$

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

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

11. (b) Velocity constant 'K' is characteristic constant of a reaction and depends only on temperature and catalyst.

12. (d) Unit of K for I$^{\text{st}}$ order reaction is $Time^{-1}$.

13. (a) $K=Ae^{-E_a/RT}$ by this equation it is clear that rate constant of a reaction depends on temperature

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

$t=2\times10^2$, $a=800$, $a-x=50$

$$k=\frac{2.303}{2\times10^2}\log_{10}\frac{800}{50}=\frac{2.303}{2\times10^2}\log_{10}16$$

$$=\frac{2.303}{2\times10^2}\log_{10}2^4=\frac{2.303}{2\times10^4}\times4\times0.301$$

$$=1.38\times10^{-2}\ s^{-1}$$

15. (d) Rate of reaction is quadrupled on doubling the concentration. Thus $r\propto[A]^2$.

16. (d) K is not constant for all the reaction.

19. (c) Rate determining step is a slow step by which rate of reaction can be determined.

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

21. (b) For reversible reaction rate constant is also reverse.

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

24. (d) Rate $= K(N_2O_5)$ hence

$2.4\times10^{-5} = 3.0\times10^{-5}(N_2O_5)$

or $(N_2O_5) = 0.8\ mol\ l^{-1}$

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

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

26. (a) Rate law for the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$

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

28. (c) Rate constant depends on temperature only.

29. (c) According to Arhenius concept

Rate constant $K = A_e^{-E_a/RT}$, Hence rate constant depends only upon temperature of the system.

30. (d) For $2A + B \rightarrow C$

Rate $= K[A][B]$

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

31. (d) The specific rate constant of a first order reaction depends upon the temperature of reaction.

32. (c) Unit of K for first order reaction $= sec^{-1}$

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

36. (c) The unit of K for zero order reaction

$= mole\ litre^{-1} sec^{-1}$.

37. (c) Order of reaction is sum of the power raised on concentration terms to express rate expression.

38. (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.

39. (c) $r = K[A]^m$ also $2r = K[4A]^m$, $\frac{1}{2} = \left(\frac{1}{4}\right)^m$

$\therefore m = \frac{1}{2}$

40. (b) $K = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$ gives constant value of K. With the given date. Hence it is 1st order.

42. (d) $r = K[A]^n$, $100r = K[10A]^n$

Thus $\frac{1}{100} = \left(\frac{1}{10}\right)^n$ or $n = 2$

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

44. (c) Inversion of cane sugar is a Pseudo unimolecular reaction.

45. (c) For 1st order reaction

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

46. (a) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2\times10^{-4}} = 1117.7\ sec.$

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

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

$\therefore T = 58.2\ min.$

48. (b) Order of reaction $= \frac{3}{2} + \frac{3}{2} = \frac{3+3}{2} = \frac{6}{2} = 3$

49. (c) Two molecules are taking part in elementary step.

50. (b) Because two molecules are taking part in elementary step.

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

52. (a) It is a first order reaction as is clear from rate law expression, $r = k(H_2O_2)$

53. (a) For Ist order reaction half life is independent of concentration.

54. (d) $K = \frac{1}{t}\log e\left(\frac{a}{a-x}\right) = \frac{1}{15}\log e\left(\frac{35}{35-9}\right)$

$= \frac{1}{15}\log e\left(\frac{35}{26}\right)$

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

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

57. (d) $Rate = K(sugar)(H_2O)^o$

58. (b) Derive $t_{1/2}$ from $K_t = 2.303\log\frac{a}{a-x}$, putting $t = \frac{1}{2}$ and $x = \frac{a}{2}$. Therefore it is $\frac{0.693}{K}$.

59. (b) $r \propto [X]^2$ or $r = k[X]^2$

60. (b) $t_{1/2} = \frac{0.693}{k}, \frac{0.693}{1.1\times10^{-9}} = 6.3\times10^8\ sec.$

61. (c) $t_{1/2} \propto \frac{1}{(a)}$ for II order reaction.

62. (d) Order of reaction is an experimental value, while molecularity is a theoretical value.

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

64. (b) $R = K[A][B]^0$ so molecularity is two and order is two.

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

66. (d) $t_{1/2} \propto \frac{1}{(a)^{n-1}}$

67. (b) $t_{1/2} \propto \frac{1}{(C_o)^{n-1}}$ $\therefore$ reaction is of first order.

68. (c) For Ist order reaction half life is independent of concentration.

69. (c) $K = \frac{0.693}{t_{1/2}}$, $K = \frac{0.693}{138.6 \text{ min}} = 0.005 \text{ min}^{-1}$

70. (b) $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

It is a pseudo-unimolecular reaction.

71. (d) $t_{1/2} \propto \frac{1}{K}$ and $K \propto t$

73. (b) For zero order reactions $\frac{dx}{dt} = K(A)^o$

74. (b) It is an bimolecular and second order reaction.

75. (d) $\frac{dx}{dt} = (HI)^2$, then order of reaction = 2

76. (b) Rate = $K(\text{Sucrose})(H_2O)^o$

77. (b) Because in this reaction one molecule of N_2O_5 is used.

78. (c) Integrated velocity equation for first order reaction is: $k = \frac{2.303}{t} \log \frac{(A)_o}{(A)}$

80. (c) $t_{1/2} = \frac{2.303 \log 2}{K} = \frac{0.693}{K}$

81. (b) Inversion of sugar is a pseudo-unimolecular reaction.

82. (b) For Ist order reaction

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

$y = c + mx$

83. (c) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.46 \times 10^{-3}} = 200 \, min$

84. (a) $\frac{1}{Time} \times (conc.) = \frac{moles \ l^{-1}}{Time} = moles \ l^{-1} time^{-1}$ for zero order reaction.

85. (a) The order of reaction is $\frac{3}{2}$ and molecularity is 2.

87. (c) Molecularity can never be fractional.

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

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

90. (c) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.35} = 9.99 \times 10^{-3} = 0.01 \, s^{-1}$

91. (b) $k = \frac{0.693}{24} hr^{-1} = \frac{2.303}{96} \log \frac{10}{a-x}$

or $\log \frac{10}{a-x} = 1.2036$ or 1 – log (a – x) = 1.2036

or $\log(a-x) = -0.2036 = \bar{1}.7964$

or $(a-x) = \text{antilog } \bar{1}.7964 = 0.6258 \, gm$

92. (b) $0.08 \, mol \, l^{-1}$ to $0.01 \, mol \, l^{-1}$ involves 3 half-life. So the t is 30 minutes

93. (c) $t_{1/2}$ of II order reaction is inversely proportional to initial concentration of reactants.

94. (b) As $r = k(H_2O_2)$, it is a reaction of 1st order.

97. (b) $r = k(C_A)^{3/2}(C_B)^{-1/2}$

Order = $\frac{3}{2} + \left(-\frac{1}{2}\right) = \frac{2}{2} = 1$

98. (c) If $\text{rate} = K(A)^m(B)^n$, then order of reaction $= m + n$.

99. (a) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100 \text{ sec}} = 6.93 \times 10^{-3} sec^{-1}$

100. (c) $t_{1/2} = \frac{0.693}{k}$

101. (b) $t_{1/2} = \frac{0.693}{k}$, $k = \frac{0.693}{480} = 1.44 \times 10^{-3} \text{ sec}^{-1}$.

102. (d) $r = k(A)^2$, when concentration is doubled

$r = k(2A)^2 = k \, 4(A)^2$ the rate becomes 4 times.

103 (c) $r = K[FeCl_3]^2[SnCl_2]^1$. Order $= 2 + 1 = 3$

105. (a) $t_{1/2}$ for I order reaction independent of initial concentration.

107. (a) The rate will be given by slowest step. Thus $r = K[A][B_2]$. $K_c = \frac{[A][A]}{[A_2]}$ or $[A] = [K_c]^{1/2}[A_2]^{1/2}$

$r = K \times [K_c]^{1/2}[A_2]^{1/2}[B_2] = K[A_2]^{1/2}[B]$. Thus order is $0.5 + 1 = 1.5$

108. (b) For Ist order reaction half life is independent of concentration.

110. (b) Rate = $K[A]^{1/2}[B]^{3/2}$

$\therefore O.R. = \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$

112. (d) The rate of this photochemical reaction is independent of the concentration, therefore, it is zero order reaction.

113. (b) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.6932\ hr^{-1}} = 1\ hr$.

114. (b) The unit of rate constant shows that reaction is of first order. For first order reaction, half life is independent of initial conc. of the reactant. Thus,

$$t_{1/2} = \frac{0.693}{0.69 \times 10^{-1}} = \frac{0.693 \times 60}{0.69 \times 10^{-1}} = 600 \text{ sec}$$

115. (d) *Given* : Rate constant of the first order reaction $(K) = 3 \times 10^{-6}$ per sec and initial concentration $[A] = 0.10 M$. We know that initial rate constant

$$K[A] = 3 \times 10^{-6} \times 0.10 = 3 \times 10^{-7} ms^{-1} .$$

116. (d) It is the characteristic of pseudo-unimolecular reactions.

117. (b) It is a second order reaction.

118. (d) $r = K$ [reactant]

$$\therefore K = \frac{1.0 \times 10^{-2}}{0.2} = 0.05$$

$$t_{1/2} = \frac{0.693}{0.05} = 13.86\ s$$

119. (a) For first order reactions rate is depend on the concentration of one reactant.

120. (b) Molecularity of a reaction never become zero or fraction.

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

$$t = \frac{2.303}{1.155 \times 10^{-3}} \log \frac{100}{100 - 50} = 600 \text{ sec}$$

122. (b) Rate = $K[A]^{3/2}[B]^{-1}$

$$\therefore O.R. = \frac{3}{2} + (-1) = \frac{1}{2}$$

123. (d) $t_{1/2} \propto (CO)^o$ *i.e.* half life for Ist order is independent of initial concentration.

124. (c) $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$

Rate = $K[NO]^2[Cl_2]^1$, $\therefore O.R. = 2 + 1 = 3$

125. (d) $8 \times 10^{-5} = \frac{1}{t}\left[\frac{1}{0.5} - \frac{1}{1}\right]$; $8 \times 10^{-5} = \frac{1}{t}[2 - 1]$

$$t = \frac{1}{8 \times 10^{-5}} = 0.125 \times 10^5 = 1.25 \times 10^4 min.$$

126. (b) $r = k[\text{reactant}]^{-1}$ $\therefore k = \frac{0.693 \times 10^{-2}}{1}$ also

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.693 \times 10^{-2}} = 100 \text{ min} .$$

127. (d) $t_{1/2} = \frac{1}{Ka}$ for second order reactions.

128. (d) $k = \frac{2.303}{t} \log\left(\frac{a}{a - x}\right)$; $k = \frac{2.303}{30} \log\left(\frac{100}{100 - 75}\right)$

$k = \frac{2.303}{t} \log\left(\frac{100}{100 - 93.75}\right)$ Put the value of K from above equation we get the value of t therefore $\therefore$ $t = 60 \text{ min}$.

129. (b) $k = \frac{0.693}{45} \text{min}^{-1} = \frac{2.303}{t_{99.9\%}} \log \frac{a}{a - 0.999a}$ or

$$t_{99.9\%} = \frac{2.303 \times 45}{0.693} \log 10^3 = 448 \text{ min} \approx 7.5\ hrs$$

130. (a) Given A(a) = 2.00 *m*, t = 200 *min* and a(a-x) = 0.15 *m* we know

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{200} \log \frac{2.00}{0.15}$$

$$= \frac{2.303}{200} \times (0.301 + 0.824) = 1.29 \times 10^{-2} \text{ min}^{-1}$$

131. (a,c) The unit for zero order reaction is $mol\ litre^{-1} time^{-1}$

132. (c) It is a third order reaction because

$\text{Rate} = \text{K[NO]}^2[O_2]^1$ $\therefore O.R. = 2 + 1 = 3$

133. (d) Order of a reaction is decided by relative concentration of reactants.

134. (c) Unit of rate constant for second order reaction is $mol^{-1} litre\ time^{-1}$

135. (a) $R = K[A]^2[B]$ order of reaction $= 2 + 1 = 3$

136. (a) Units of 1st rate constant order reaction are sec^{-1} and for zero order reaction, these are $mol\ litre^{-1}\ sec^{-1}$ *i.e.* $M\ sec^{-1}$.

137. (c) This reaction is bimolecular and first order of reaction.

138. (c) $t_{1/2} = \frac{0.693}{k}$ Given $t_{1/2} = 693$ sec

$$693 = \frac{0.693}{k},\ k = \frac{693 \times 10^{-3}}{693} ;\ k = 10^{-3} = 0.001 \text{ sec}^{-1} .$$

139. (d) $2A + B \rightarrow C + B$

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

$\therefore O.R. = 2 + 1 = 3$ and molecularity is $3[2A + B]$.

140. (c) In photochemical reactions the rate of reaction is independent of the concentration of reacting species.

141. (c) We know that $k = \frac{2.303}{t} \log \frac{a}{a - x}$

$$10^{-3} = \frac{2.303}{t} \log \frac{a}{(a - \frac{2a}{3})},\ 10^{-3} = \frac{2.303}{t} \log 3$$

$$10^{-3} = \frac{2.303}{t} \times 0.4771,\ t = \frac{2.303 \times 0.4771}{10^{-3}} = 3300 \text{ sec}$$

142. (c) $R = K(A)^2$, $R' = K(2A)^2$, $\therefore \frac{R'}{R} = 4$

$R = K(A)^2,\ R' = K(3A)^2,\ \frac{R'}{R} = 9$

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

$k = \frac{2.303}{32}\log\left(\frac{100}{100-75}\right)$ .... (i)

$k = \frac{2.303}{t}\log\left(\frac{100}{100-50}\right)$ ....(ii)

from the two equation (i) and (ii), $t = 16$ minutes.

146. (c) The relation between half - life period and initial concentration (c) for a n^th^ order reaction is given by $t_{1/2} \propto \frac{1}{C^{n-1}}$ for first order reaction $(n = 1)$. $t_{1/2} \propto \frac{1}{C^{1-1}}$ or $t_{1/2} \propto C^0$.

147. (c) $R = k[NO]^2[O_2]$, $R' = k[2NO]^2[2O_2]$

$R' = k \times 4[NO]^2[O_2] = k \times 8[NO]^2[O_2]$

$\frac{R'}{R} = \frac{k \times 8[NO]^2[O_2]}{k[NO]^2[O_2]} = 8$

148. (b) For zero order reaction $r = k$.

149. (b) $k = \frac{2.303}{t}\log\frac{0.8}{0.6} = 2.303\log\frac{4}{3}$

$t = \frac{2.303}{k}\log\frac{0.9}{0.675} = \frac{2.303}{k}\log\frac{4}{3}$; $t = 1$ *hour*.

150. (a) For zero order reaction

Velocity constant $= \frac{dx}{dt} = \frac{\text{Concentrat ion}}{\text{Time}}$

Unit $=$ concentrat ion $\times$ time^{-1}.

151. (d) $H_2 + Br_2 \rightleftharpoons 2HBr$ is a 1.5 order reaction

i.e., $K = [H_2][Br_2]^{1/2}$.

152. (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.

153. (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, $t = \frac{2.303}{K}\log\frac{a}{a-x} = \frac{2.303}{.693} \times 10 \times \log\frac{10}{5}$

$= \frac{2.303 \times 10 \times \log 2}{.693} = \frac{2.303 \times 10 \times 0.301}{0.693} = 10$ years.

154. (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 0.1*m* to 0.025 will fall in 2 half lives so total time taken $= 2 \times T_{1/2} = 2 \times 15 = 30$ *min*.

155. (c) $K = \frac{2.303}{1\ hr}\log\frac{100}{25} = \frac{2.303}{t}\log\frac{100}{50}$

$\therefore\ \log 4 = \frac{1}{t}\log 2$

$\therefore\ 2\log 2 = \frac{1}{t}\log 2$; $t = \frac{1}{2}hr$.

156. (b) $x_{(g)} \rightarrow y_{(g)} + z_{(g)}$

The reaction is a first order reaction hence,

$K = \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{0.693}{10\text{ min}}$

$= \frac{2.303}{t}\log\frac{a}{a/10} = \frac{0.693}{10} = \frac{2.303}{t}\log 10$

$\therefore\ t = \frac{2.303 \times 10}{.693} = 33\text{ min}$.

157. (a) For the first order reaction $t = \frac{2.303}{K}\log\frac{a}{a-x}$

Given: $a = 0.5\ mol/litre$; $a - x = 0.05\ ,mol/litre$

$K = 6\sec^{-1}$.

$t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6}\log 10 = \frac{2.303}{6} = 0.384\text{ sec}$.

158. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

159. (d) Rate $\left(\frac{dx}{dt}\right) = K.c$; $1.5 \times 10^{-2} = K \times 0.5$

For first order $K = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}\ \text{min}\,ute^{-1}$

$t_{1/2} = \frac{.693}{K} = \frac{.693}{3 \times 10^{-2}} = 23.1\ \text{min}\,ute$.

160. (c) For first order reaction $K = \frac{2.303}{t}\log\frac{a}{a-x}$

Given: $a = \frac{1}{10} = .1m$; $a - x = \frac{1}{100} = .01m$; t = 500 *sec*

$\therefore\ K = \frac{2.303}{500}\log\frac{.10}{.01} = \frac{2.303}{500}\log 10$

$= \frac{2.303}{500} = 0.004606 = 4.6 \times 10^{-3}\sec^{-1}$.

161. (b) For zero order reaction, rate of reaction is independent of concentration $R = K[\text{Reactant}]^0$

162. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

163. (b) $t_{1/2} \propto a^{1-n} \Rightarrow \frac{0.1}{0.4} = \frac{(200)^{1-n}}{(50)^{1-n}} \Rightarrow \frac{1}{4} = \left[\frac{4}{1}\right]^{1-n} = \left[\frac{1}{4}\right]^{n-1}$

$\Rightarrow \frac{1}{4^1} = \frac{1}{4^{n-1}} \quad \therefore\ n-1=1;\ n=2$.

164. (abd) By Vant's Hoff equation, $\frac{d\ln k}{dt} = \frac{\Delta H^o}{RT^2}$

or $\ln k_p = -\frac{\Delta H^o}{RT} + I$. Hence (a) is correct (b) is also correct as plot of log (X) vs time is linear. (c) is wrong because $p \propto T$ at constant volume. (d) is correct by Boyle's law.

165. (ad) (a) is correct because degree of dissociation $= 1 - e^{-kt}$ at any time *t*.

(b) is wrong because plot of log [A] vs *t* is a straight line

(c) is wrong because time taken for 75% reaction is two half life.

(d) is correct because in $k = Ae^{-E_a/RT}$, $E_{a/RT}$ is dimensionless hence *A* has the unit of *K*.

166. (b) $aA \rightarrow xP$

Rate of reaction = $[A]^a$

Order of reaction = *a*

$[A]_1 = 2.2\ mM$, $r_1 = 2.4\ m\ M\ s^{-1}$ ...(i)

$[A]_2 = 2.2/2\ mM$, $r_1 = 0.6\ m\ M\ s^{-1}$ or, $\frac{2.4}{4}$ ...(ii)

On reducing the concentration of *A* to half, the rate of reaction is decreased by four times.

Rate of reaction = $[A]^2$

Order of reaction = 2.

167. (d) Order of a reaction can be fractional.

168. (b) $t_{1/4} = \frac{2.303}{K}\log\frac{1}{1-\frac{1}{4}} = \frac{0.29}{K}$.

169. (d) $R = K[A]$

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

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

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

170. (b) $R = k[B]^n$; $\frac{1}{4}R = k[2B]^n$; $4 = \left(\frac{1}{2}\right)^n$; $4 = 2^{-n}$; $n = -2$.

171. (c) $T = t_{1/2}\times n$ *i.e.* $12 = 3\times n \Rightarrow n = 4$

$N = N_0\left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

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

$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.7}\times10^5 = 11.32h$

173. (c) $A + B \rightarrow C$

On doubling the concentration of *A* rate of reaction increases by four times. Rate $\propto [A]^2$

However on doubling the concentration of *B*, rate of reaction increases two times. Rate $\propto [B]$

Thus, overall order of reaction = 2 + 1= 3.

174. (a) In case of zero order reaction, the concentration of reactant decreases linearly with time, as its rate is independent of the concentration of the reactants.

Collision theory, Energy of activation and Arrhenius equation

1. (b) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

2. (b) All collisions are not effective and does not result in the formation of the products

3. (b) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

4. (c) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

5. (a) Slower reaction rate indicates higher energy of activation.

6. (d) Energy of activation decreases, rate of reaction will increases.

7. (d) Number of collision depend upon pressure, concentration and temperature.

9. (c) The definition of activation energy.

10. (b) Activation energy is the energy needed by reactant molecules to gain threshold energy level.

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

12. (d) Increase in the rate of reaction is determined by the increase in the number of effective collisions.

13. (a) Energy of activation reduced by increasing temperature.

14. (d) The definition of threshold energy.

15. (a) The definition of activation energy.

16. (b) When the temperature is increased, heat energy is supplied which increases the kinetic energy of the reacting molecules. this will increase the number of collisions and ultimately the rate of reaction will be enhanced.

17. (d) In exothermic and endothermic reactions will be more and less than E_a respectively.

19. (b) The value of activation energy for a chemical reaction primarily dependent on the nature of reacting species.

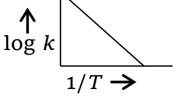
20. (a) Arrhenius equation is $\log k = \log A - \frac{E_a}{RT}$

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

24. (b) When $E_a = 0$ rate constant is independent of temperature.

25. (a) It is modified form of Arrhenius equation.

28. (b) A graph plotted between $\log k$ Vs$\frac{1}{T}$ for calculating activation energy is shown as from Arrhenius equation



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

30. (c) It is Arrhenius equation.

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

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

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

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

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

32. (d) When $E_a = 0$, the rate of reaction becomes independent of temperature.

(E_a = Energy of activation).

33. (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. ($e \approx 2.7$).

34. (c) Endothermic reactions are those which involve absorption of heat. High activation energy means potential energy of product must be much greater than reactants.

35. (a) For endothermic reaction $\Delta H = +ve$

Then from equation $\Delta H = E_{a_{F.R.}} - E_{a_{B.R.}}; E_{B.R.} < E_{F.R.}$

36. (a) Arrhenius suggested an equation which describes rate constant (K) as a function of temperature.

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

$$\ln K = \ln A - e^{E_a/RT}$$

Photochemical reactions

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

3. (c) Stark - Einstein was given the law of photochemical equivalence.

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

Critical Thinking Questions

1. (a) For the given reaction :

$$-\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

2. (c) $-\frac{1}{3}\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} \quad \therefore \frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$

3. (a) Concentration of reactants decreases while concentration of product increases.

4. (d) $R = K(A)^n(B)^m$

$$R' = K(2A)^n\left(\frac{B}{2}\right)^m = K(A)^n 2^n (B)^m 2^{-m}$$

$$= K(A)^n(B)^m 2^{n-m}, \frac{R'}{R} = \frac{K(A)^n(B)^m 2^{n-m}}{K(A)^n(B)^m} = 2^{n-m}$$

5. (c) $\ln K = \ln\ -\frac{E_a}{RT}$ is Arrhenius equation. Thus plots of ln K vs 1/T will give slope $= -E_a/RT$ or $-E_a/2.303\,R$.

6. (c) For a reaction E_a for forward reaction $= E_a$ for backward reaction + ΔH.

7. (c) As $K^{'} > K^{''}, E_a^{'} < E_a^{''}$ (Greater the rate constant, less is the activation energy).

8. (b) $T_2 = T(say), T = 25^o C = 298\,K,$

$$E_a = 104.4\ \text{kJ}\ mol^{-1} = 104.4 \times 10^3\ \text{J}\,mol^{-1}$$

$$K_1 = 3 \times 10^{-4},\ K_2 = ?,$$

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{K_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3\text{J}\ mol^{-1}}{2.303 \times (8.314\ \text{J}\ k^{-1}\ mol^{-1})}$$

$$\left[\frac{1}{298\,K} - \frac{1}{T}\right] \text{As T} \to \infty, \frac{1}{\text{T}} \to 0$$

$$\therefore \log\frac{K_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3\ \text{J}\ mol^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log\frac{K_2}{3 \times 10^{-4}} = 18.297, \frac{K_2}{3 \times 10^{-4}} = 1.98 \times 10^{18} \text{ or}$$

$$K_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14}\,s^{-1}$$

9. (a) Because reaction is exothermic

10. (d) $k = Ae^{-E^0/RT}$ $\underset{y}{\log\ K} = \underset{c}{\log\ A} - \underset{mx}{E^o/RT} \therefore \log\ K\ \ Vs\ \frac{1}{T}$.

11. (c) $\log\frac{K_2}{K_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

12. (a) $2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$$\log \frac{K_2}{K_1} = \frac{9.0 \times 10^3}{2.303 \times 2}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$\frac{K_2}{K_1} = 1.63\,;\; K_2 = 1.63\,K_1;\frac{1.63K_1 - K_1}{K_1} \times 100 = 63.0\%$$

13. (d) Combustion is an exothermic process, which is expected to be favoured by low temperature, but it is not true. Combustion include burning of particles which takes place at higher temperature. Thus at high temperature due to combustion of more particles, the reaction proceeds at higher rate.

14. (d) Rate constant $= 2.3 \times 10^{-2}\ \text{sec}^{-1}$

It means it is a first order reaction (because unit of rate constant is sec^{-1})

For first order reaction $K = \frac{1}{t}\ln\frac{a}{a-x}$

$$Kt = \ln\frac{a}{a-x} = \ln\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

15. (b) Because as reaction progresses the amount of acetic acid increases.

16. (d) Half life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is 4.

17. (a) It is similar to $y = mx + c$

18. (b) $r = K[A]^n$, $100r = K[10A]^n$

Thus $\frac{1}{100} = \left(\frac{1}{10}\right)^n$ or $n = 2$

19. (c) Concentration will fall from 0.1 *M* concentration to 0.025 *M* concentration within 2 half lives.

$2 \times T_{1/2} = 40\ min$

$\therefore\ T_{1/2} = 20\ \ min$

Rate of reaction = *K* . c $= \frac{0.693}{T_{1/2}}.c$

$$= \frac{0.693}{20} \times 10^{-2} M/\text{min} \quad = 3.47 \times 10^{-4} M/\text{min}^{-1}.$$

20. (e) % distribution of $B = \frac{K_1}{K_1 + K_2} \times 100$

$$= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-4}} \times 100$$

$B\% = 76.83\%$

$\%\text{Distribution of } C = \frac{K_2}{K_1 + K_2} \times 100$

$$= \frac{3.8 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-4}} \times 100$$

$C\% = 23.17\%$

Assertion and Reason

1. (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.

2. (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.

3. (b) For a zero order reaction, $t_{1/2} = [A_0]/2K$.

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

6. (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 $x = a/2$, $t = t_{1/2}$

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

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

7. (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.

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

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

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

11. (a) Rate expression $\frac{dx}{dt} = K[A]^m[B]^n$

Shows that the total order of reactions is $m + n + O \quad = m + n$ 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.

Chemical Kinetics

SET Self Evaluation Test -11

1. The temperature coefficient of most of the reactions lies between **[MP PET 1999]**

(a) 1 and 3 (b) 2 and 3

(c) 1 and 4 (d) 2 and 4

2. The influence of temperature on the rate of reaction can be found out by **[AFMC 2001]**

(a) Clapeyron–Claussius equation

(b) Gibbs–Helmholtz equation

(c) Arrhenius equation

(d) Vander Waal's equation

3. The mechanism for the reaction is given below

$2P + Q \rightarrow S + T$

$P + Q \rightarrow R + S$ (slow)

$P + R \rightarrow T$ (fast)

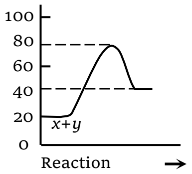
The rate law expression for the reaction is

[Kurukshetra CEE 2002]

(a) $r = k[P]^2[Q]$ (b) $r = k[P][Q]$

(c) $r = k[A][R]$ (d) $r = k[P]^2$

4. Consider the following energy profile for the reaction. $X + Y = R + S$. Which of the following deductions about the reaction is not correct



(a) The energy of activation for the backward reaction is 80 *kJ*

(b) The forward reaction is endothermic

(c) ΔH for the forward reaction is 20 *kJ*

(d) The energy of activation for the forward reaction is 60 *kJ*

5. The minimum energy required for molecules to enter into the reaction is called

[KCET 1986; EAMCET 1992; MP PMT 1993; MP PET 1994]

(a) Potential energy

(b) Kinetic energy

(c) Nuclear energy

(d) Activation energy

6. The minimum energy necessary to permit a reaction is

[NCERT 1989]

(a) Internal energy

(b) Threshold energy

(c) Activation energy

(d) Free energy

7. The formation of gas at the surface of tungsten due to adsorption is the reaction of order**[AIEEE 2002]**

(a) 0

(b) 1

(c) 2

(d) insufficient data

8. The time of completion of 90% of a first order reaction is approximately

(a) 1.1 times that of half life

(b) 2.2 times that of half life

(c) 3.3 times that of half life

(d) 4.4 times that of half life

9. In a photochemical reaction, the ratio of number of dissociate molecules and number of quanta of absorbed energy is called

(a) Einstein

(b) Quantum efficiency

(c) Quantum constant

(d) Planck constant

10. A reaction rate constant is given by

$k = 1.2 \times 10^{14}\, e^{-(25000/RT)}\, \sec^{-1}$

It means **[MP PET 1995]**

(a) $\log k$ versus $\log T$ will give a straight line with slope as – 25000

(b) $\log k$ versus T will give a straight line with slope as – 25000

(c) $\log k$ versus $\log 1/T$ will give a straight line with slope as – 25000

(d) $\log k$ versus $1/T$ will give a straight line

Answers and Solutions

(SET -11)

1. (b) Temperature coefficient = $\frac{K_{35^o C}}{K_{25^o C}}$ = between 2 and 3.

2. (c) Arrihenius equation is : $K = Ae^{-E_a/RT}$

3. (b) The rate law expression for the reaction is $r = k[P][Q]$.

4. (a) E_a of backward reaction $= 80 - 40 = 40 kJ$

Hence (a) statement is wrong.

5. (d) The energy necessary for molecules to undergoes chemical reaction is known as Activation energy.

6. (b) Molecules undergoing reaction should cross over the minimum energy barrier or energy level known as threshold energy.

7. (a) The order of reaction for the formation of gas at the surface of tungsten due to adsorption is zero .

8. (c) For a first order reaction

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

$$t = \frac{2.303}{k}\log\frac{100}{(100-90)} = \frac{2.303 \times t_{1/2}}{0.593} \times \log\frac{100}{10}$$

$$= 3.3 \times t_{1/2} \times \log 10 = 3.3\ t_{1/2}$$

9. (b) It is also known as Quantum yield and indicated by ϕ .

10. (d) According to the Arrihenius equation a straight line is to be `obtained by plotting the logarithm of the rate constant of a chemical reaction (log K) against $1/T$.

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