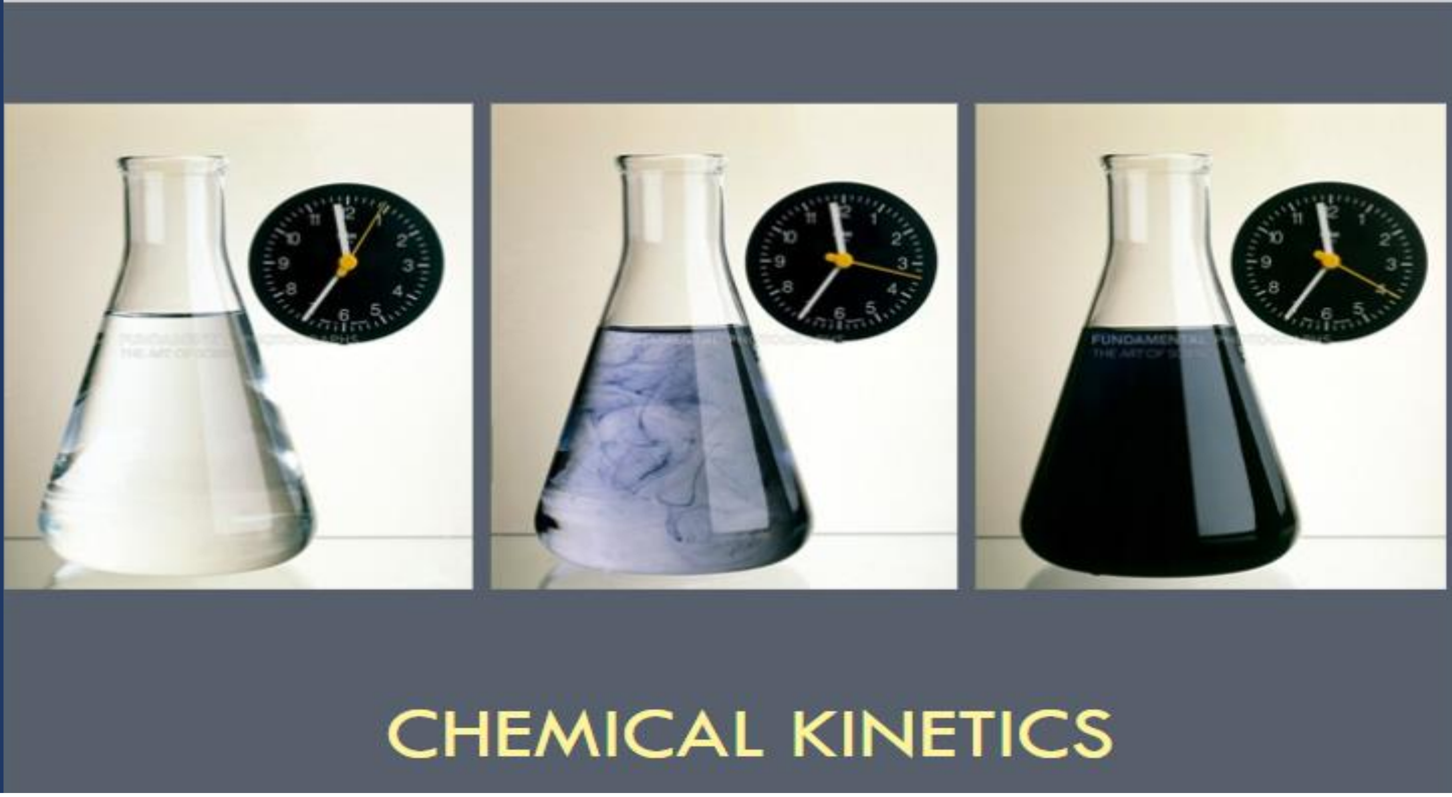


CHAPTER – 4

CHEMICAL KINETICS

Chemical kinetics:

The chemical component responsible for the chemical reaction rate, the factors that affect the reaction rate and the reaction process is called chemical kinetics.

Chemical reactions on the basis of the reaction rate

Fast/instantaneous reaction - a chemical reaction that dissipates in less time than Ips, known as a rapid reaction. It is almost impossible to measure the speed of such a reaction, e.g. ionic reaction, organic substitution reaction.

Slow reaction - a chemical reaction that lasts a long time from certain minutes to certain years is called a slow reaction e.g. metal rust, diamond conversion etc.

Moderately slow reaction - The chemical reaction between a slow and rapid reaction is called a moderate slow reaction.

Rate of reaction:

The reaction rate or reaction rate is the rate at which a chemical reaction occurs, defined as an increase in the concentration of the product during the unit and a decrease in the concentration of the reactant during each unit. It is expressed in mol / L / s or M / s or atm / timeunits.

For a Chemical Reactions:

$aA + bB \rightarrow cC + dD$

Average rate of reaction (rav) =

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

Rate of disappearance of

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

When d [A] is a slight change in conc. of 'A' and dt is a minimal time interval.

Disappearance rate of

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

When d [B] is a minor change in conc. of 'B' and dt is a minimal time interval.

Disappearance rate of

$$C = \frac{+d[C]}{dt}$$

When d [C] is a slight change in conc. of 'C' and dt is a minimal time interval.

Disappearance rate of

$$D = \frac{+d[D]}{dt}$$

When d [D] is a minor change in conc. of 'D' and dt is a minimal time interval.

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

Factor affecting rate of reaction:

Nature and focus of reaction.
Temperature.
More response area.
Radiation and catalyst.
Gas pressure.

Nature of the reaction

- The rate of reaction highly depends on the type and nature of the reaction. As mentioned earlier, few reactions are naturally faster than others while some reactions are very slow.
- The physical state of reactants, number of reactants, complexity of reaction and other factors highly influence the reaction rate as well.
- The rate of reaction is generally slower in liquids when compared to gases and slower in solids when compared to liquids. Size of the reactant also matters a lot. The smaller the size of reactant, the faster the reaction.

Effect of concentration on reaction rate

- According to the collision theory, the rate of reaction increases with the increase in the concentration of the reactants.
- As per the law of mass action, the chemical reaction rate is directly proportional to the concentration of reactants.
- This implies that the chemical reaction rate increases with the increase in concentration and decreases with the decrease in the concentration of reactants.
- Time plays a major role in changing the concentration of reactants and products. Therefore, even time is a vital factor affecting the reaction rate.

Temperature

- According to collision theory, a chemical reaction that takes place at a higher temperature generates more energy than a reaction at a lower temperature.
- This is because colliding particles will have the required activation energy at high temperature and more successful collisions will take place.
- There are some reactions that are independent of temperature. Reactions without an activation barrier are examples of chemical reactions that are independent of temperature.

Pressure factor

- Pressure increases the concentration of gases which in turn results in the increase of the rate of reaction. The reaction rate increases in the direction of less gaseous molecules and decreases in the reverse direction.
- Thus, it can be understood that pressure and concentration are interlinked and that they both affect the rate of reaction.

Characteristics of rate constant:

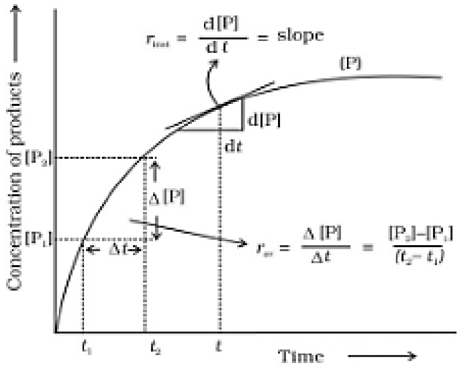
- It has a fixed number of reactions given at a given temperature
- Its value increases with increasing temperature
- The amount does not depend on the initial focus
- Rapid reactions have higher fixed rate values
- Its unit depends on the time unit and concentration and response order

Average rate:

It is a measure of how much work has changed for each unit, on average, over time. It is based on the slope of a straight line that connects the intermittent ends to the activity graph.

$$\text{Average rating} = \frac{\Delta x}{\Delta t}$$

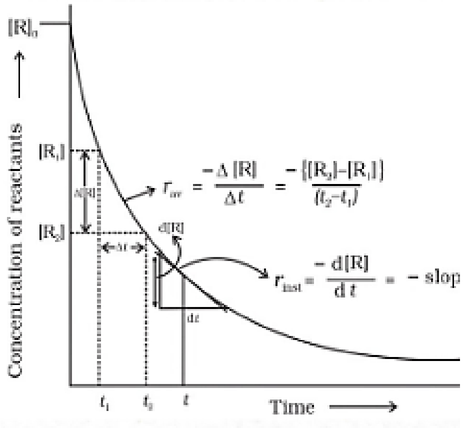
The average level of the change formula is used to determine the slope of a graph function. To find the average value of a change, divide the change in y values by the change in x values.



Instantaneous rate:

A quick measure is a measure over a period of time. Quick rate is different: -d [reactant] / dt or d [product] / dt. We determine the acceleration rate during t: by calculating the negative slope angle of the reactant concentration compared to the t time.

Instantaneous rate = dx / dt



Rate of appearance and rate of disappearance:

Let us consider a reaction R → P

At time t_1: R_1 P_1

T_2: R_2 P_2

rate of appearance of R = decrease in [R]/time taken= - $\Delta[R]/\Delta t$
rate of appearance of P = increase in [P]/time taken = $\Delta[P]/\Delta t$

Example

$Hg_{(l)} + Cl_{2\,(g)} \rightarrow HgCl_{2\,(s)}$
Rate of reaction = rate of disappearance of Hg/Cl_2 = rate of appearance of $HgCl_2$
$= -\Delta[Hg]/\Delta t = -\Delta[Cl_2]/\Delta t = \Delta HgCl_2]/\Delta t$

Note: if stoichiometric coefficient of reactants or products are not equal to one, then rate of disappearance of any of the reactants or rate of appearance of products is divided by their respective stoichiometric coefficient.
aA + bB → cC + dD
rate of reaction = $-1/a\,\Delta[A]/\Delta t = -1/b\,\Delta[B]/\Delta t = 1/c\,\Delta[C]/\Delta t = 1/d\,\Delta[D]/\Delta t$

Rate constant:

A fixed rate, or a certain fixed rate, a fixed rate that reflects the relationship between the rate of chemical reactions and the concentration of the reactors.

The 'k' equity is known as the fixed equation.
k is the first order total value, with 1 / s units. The method of determining the order of the response is known as the initial level method. The total order of the reaction is the sum of all the parameters of the focus conditions in the measurement equation.

Rate Law:

The rate law (also known as the rate equation) for a chemical reaction is an expression that provides a relationship between the rate of the reaction and the concentrations of the reactants participating in it.

Expression

For a reaction given by:
aA + bB → cC + dD
Where a, b, c, and d are the stoichiometric coefficients of the reactants or products, the rate equation for the reaction is given by:

Rate ∝ $[A]^x [B]^y \Rightarrow$ Rate = $k[A]^x [B]^y$
where,
[A] & [B] denote the concentrations of the reactants A and B.
x & y denote the partial reaction orders for reactants A & B (which may or may not be equal to their stoichiometric coefficients a & b).

The proportionality constant 'k' is the rate constant of the reaction.

It is important to note that the expression of the rate law for a specific reaction can only be determined experimentally. The rate law expression cannot be obtained from the balanced chemical equation (since the partial orders of the reactants are not necessarily equal to the stoichiometric coefficients).

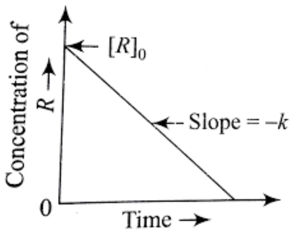
Order of reaction:

Order of reaction is the relationship between response focus and response rate. It can be defined as the dependence of the reaction rate on the concentration of all reactants.
If the expression of the reaction rate rule is Measure = k [A] × [B] y
Then its reaction order is = x + y
The order cannot be determined by the balanced chemical equation provided. It can be determined by testing.

Integrated rate law for zero order reaction: R → P

$$\frac{dx}{dt} = k[R]^0$$

$$k = \frac{[R_0] - [R]}{t}$$



If we arrange the graph between the concentrations of R vs time t, the graph is a straight line with a volume equal to -k and the equation is equal to $[R_0]$.

Q1. Identify the order of a reaction if the units of its rate constant are:
(i) L^{-1} mol s^{-1}
(ii) L mol^{-1} s^{-1}

S1. The order of the reaction is as follows-
(i) Unit = L^{-1} mol s^{-1} = It is a zero-order reaction.
(ii) Unit = L mol^{-1} s^{-1} = It is a second-order reaction.

Q2. **(a)** A reaction is second order in A and first order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected by increasing the concentration of A three times?
(iii) How is the rate affected when the concentrations of both A and B are doubled?

(b) A first-order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ for this reaction.
(Given: log $_{1.428}$ = 0.1548)

S2.
(a) A reaction is second order in A and first order in B.
(i) The differential rate equation is given by-

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

(ii) If the concentration of A is increased three times–

$$\frac{dx}{dt} = k[3A]^2[B]^1 = 9k[A]^2[B]^1$$

Hence, the rate will increase 9 times.

(iii) When the concentrations of both A and B are doubled–

$$\frac{dx}{dt} = k[2A]^2[2B]^1 = 8k[A]^2[B]^1$$

Hence, the rate will increase 8 times.

(b) $k = \frac{2.303}{t}\log\frac{[R_0]}{[R]} = \frac{2.303}{40}\log\frac{[R]_0}{\frac{70}{100}[R]_0}$

$k = \frac{2.303}{40}(log10 - log7) = \frac{2.303}{40}(1 - 0.08451)$

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

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{k} = \frac{0.693 \times 40}{2.303 \times 0.1549} = 77.7\ minutes$$

Molecularity of reaction:

Reaction molecularity is defined as the number of reaction molecules that collide simultaneously to produce a chemical reaction. In other words, the molecularity of the basic reaction is defined as the number of reaction molecules that participate in the reaction. In this reaction, the molecularity is twofold.

For example, the decay of dinitrogen tetroxide.

Difference between molecularity and order of reaction are as follows:

Molecularity	Order
Molecularity is the number of ions or molecules that take part in the rate-determining step.	Number of molecules of the reactant whose concentration changes during the chemical change
It is always a whole number	It can either be a whole number or a fraction
The molecularity of the reaction is determined by looking at the reaction mechanism	The order of the reaction is determined by the experimental methods
It is theoretical concept	It is experimental concept
It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for an overall complex reaction.	It is meant for the reaction and not for its individual steps

Note: let us consider a reaction takes place into two step:

(i) $H_2O_2 + I^- \rightarrow H_2O + IO^-$ [slow]

(ii) $H_2O_2 + IO^- \rightarrow H_2O + I^-$ [fast]

Slow step [first step] is the rate determining step [RDS]
Rate equation for the reaction can be written on the basis of RDS

Rtae = $-d[H_2O_2]/dt = k\,[H_2O_2]^1[I^-]^1$
Overall order of reaction = 1 + 1 = 2

Half-life of reaction:

Part of the life of the reaction period is the reaction time when the concentration of the reactants is halved.
In response to a zero order, the half-life is as it is

$t_{1/2} = \dfrac{[R_0]}{2k}$ For first order reaction, half-life time is

$t_{1/2} = \dfrac{0.693}{k}$ where k is rate constant.

It is independent of initial concentration for first order reaction.
Rate law for first order reaction: $R \rightarrow P$

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

where 'k' is a fixed or specific reaction rate, [Ro] is the first molar conc. [R] is the last molar conc. later 't'.

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

When we plot the graph between Ln [R] and time, we find the slope of the straight line = -k and cross the Ln $[R_0]$.

Q1. Show that the time required for half the change (half-life period) in a first-order reaction is independent of initial concentration.

S1. Half-life period $t_{1/2}$ of a reaction is defined as the time required to reduced the concentration of a reactant to one half of its initial value.

$$k_1 = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

if amount reacted x= a/2 then t = $t_{1/1}$

$$\therefore t_{1/2} = \frac{2303}{t}\ log\left(\frac{a}{s-s/2}\right)$$

$$t_{1/2} = \frac{2.303 \log(2.0)}{k_1} \Rightarrow t_{1/2} = \frac{0.693}{k_1} secs$$

Thus half-life period of a first order reaction is independent of the initial concentration of the reactant.

Q2. Rate constant is equal to the rate of reaction when molar conc. of reactants is unity. Its unit depends upon order of reaction.
A reactant has a half-life of 10 minutes. Then, calculate the rate constant for the first-order reaction.
$T_{1/2}$ = 10 minutes = 10 × 60 = 600 seconds.

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{600\ seconds}$$

$K = 1.155 \times 10^{-3} s^{-1}$

Pseudo's first order response:

It has been observed that in a particular reaction consisting of two reactants, when one of the reactant is present in excess, its concentration remains the same as it does not change during the reaction. Such a reaction is therefore said to have a pseudo-first order reaction.

OR

The first Pseudo-order reaction can be defined as a second-order or bimolecular reaction that acts as a first-order response. This reaction occurs when a single reaction is too extreme or is constantly fixed compared to another.

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$
So, in this reaction,

Rate = k [$CH_3COOC_2H_5$]
For chemical reaction,

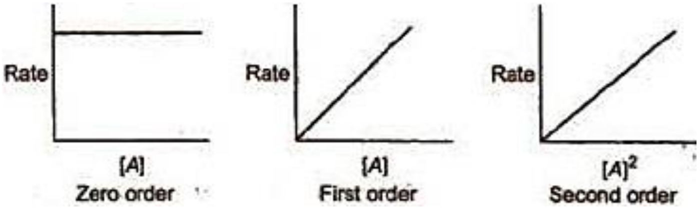
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{A} \underset{glucose}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6}$$

$$H = \frac{2.303}{t}\log\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

Ways to determine the order of the reaction:

Graphical method:

- The concentration of the reactants is measured in a specific way.
- The graph is organized between concentration and time.
- Rapid response rates at different times are calculated by finding the slopes of the tangents corresponding to different times.



Initial rate method:

In this method, the order of the reaction is determined by alternating the focus of one response while the others are kept unchanged.

Integrated rate law method:

(i) The method can be used with various sets of a, x and t with calculated combined values.
(ii) The value of k is determined and tested in all sets of a, x and t.
(iii) If the value of k does not change, the number used gives the order of reaction.
(iv) When all reactants are at the same molar level, kinetic calculations are given as follows:

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

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

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

Zero-order reaction

Zero-order reaction is a chemical reaction wherein the rate does not vary with the increase or decrease in the concentration of the reactants. Therefore, the rate of these reactions is always equal to the rate constant of the specific reactions (since the rate of these reactions is proportional to the zeroth power of reactants concentration).

Differential and Integral Form of Zero Order Reaction

The Differential form of a zero order reaction can be written as:

$$Rate = \frac{-dA}{dt} = k[A]_0 = k$$

Where 'Rate' refers to the rate of the reaction and 'k' is the rate constant of the reaction.

This differential form can be rearranged and integrated on both sides to get the required Integral form as shown below.

$$Rate = \frac{-d[A]_0}{dt} = k$$

Multiplying both sides with '-dt', we get:

$$d[A] = -kdt$$

Integrating on both sides, we get:

$$\int_{[A]_0}^{[A]} d[A] = -\int_0^t kdt$$

Where [A]0 is the initial concentration of the reactant [A] at time t=0. Solving for [A], we get:

$$[A] = [A]_0 - kt$$

Which is the required integral form. This form enables us to calculate the population of the reactant at any given time post the start of the reaction.

Half-Life of a Zero Order Reaction

The timescale in which there is a 50% reduction in the initial population is referred to as half-life. Half-life is denoted by the symbol '$t_{1/2}$'.

From the integral form, we have the following equation

$$[A] = [A]_0 - kt$$

Replacing t with half-life $t_{1/2}$ we get:

$$\frac{1}{2}[A] = [A]_0 - kt_{1/2}$$

Therefore, t1/2 can be written as:

$$kt_{1/2} = \frac{1}{2}[A]_0$$

And,

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

It can be noted from the equation given above that the half-life is dependent on the rate constant as well as the reactant's initial concentration.

Q1. A zero order reaction in A has a rate constant of 0.003 $molL^{-1}sec^{-1}$. How long will it take for A's initial concentration to fall from 0.10 M to 0.075 M?

S1. According to zero order reaction
$[A] = [AO]^{-kt}$
Where [A] is the concentration at time, t
[AO] is the concentration at time = 0
k is the rate constant
Given: [A] = 0.075 M, [AO] = 0.10 M , k = 0.003 $molL^{-1}sec^{-1}$
Time, t=?
Substitute the values in the formula of zero order reaction
0.075 = 0.10 -0.003t
t= 8.33 s

First-order reaction:

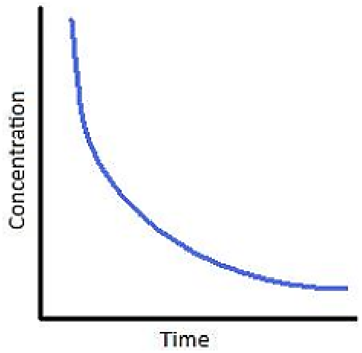
A first-order reaction can be defined as a chemical reaction in which the reaction rate is linearly dependent on the concentration of only one reactant. In other words, a first-order reaction is a chemical reaction in which the rate varies based on the changes in the concentration of only one of the reactants. Thus, the order of these reactions is equal to 1.

Example

Examples of First-Order Reactions

$SO_2Cl_2 \rightarrow Cl_2 + SO_2$

$2N_2O_5 \rightarrow O_2 + 4NO_2$



Half-Life of a First-Order Reaction

The half-life of a chemical reaction (denoted by '$t_{1/2}$') is the time taken for the initial concentration of the reactant(s) to reach half of its original value. Therefore,

At t = $t_{1/2}$, $[A] = [A]_0/2$

Where [A] denotes the concentration of the reactant and $[A]_0$ denotes the initial concentration of the reactant.

Substituting the value of $A = [A]_0/2$ and $t = t_{1/2}$ in the equation $[A] = [A]_0\, e^{-kt}$:

$$\frac{[A]_0}{2} = [A]_0 e^{-kt_{1/2}}$$

$$\Rightarrow \frac{1}{2} = e^{-kt_{1/2}}$$

Taking the natural logarithm of both sides of the equation to eliminate 'e', the following equation is obtained.

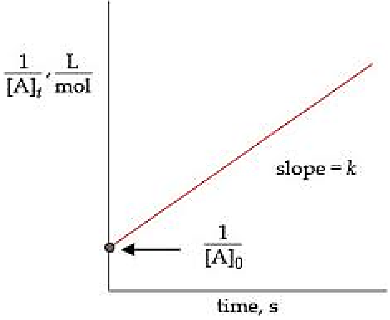
$$ln(\tfrac{1}{2}) = -kt_{1/2}$$

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

Thus, the half-life of a first-order reaction is equal to 0.693/k (where 'k' denotes the rate constant, whose units are s^{-1}).

Second-order reaction

Second order reactions can be defined as chemical reactions wherein the sum of the exponents in the corresponding rate law of the chemical reaction is equal to two. The rate of such a reaction can be written either as $r = k[A]^2$, or as $r = k[A][B]$.



Half-life period method:

This method is only used when the law of proportionality involves a single period of torture.

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

A schematic graph of log t1 / 2 vs log a provides a straight line with a slope (1-n), determining the inclination we can find the order of n. If half the life in a different focus is given,

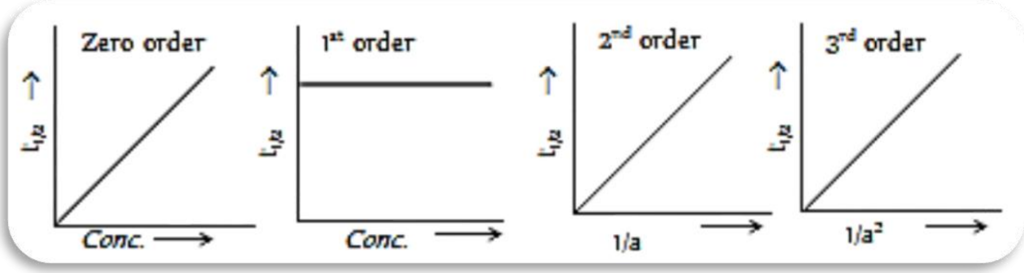
$$\left(t_{1/2}\right)_1 \propto \frac{1}{a_2^{x-1}}; \frac{\left(t_{\frac{1}{2}}\right)}{\left(t_{\frac{1}{2}}\right)_2} = \left(\frac{a_2}{a_1}\right)$$

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

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

The above relationship can be used to determine the order of the reaction n

Half-life virsus concentration (t1 / 2 µ a1-n)



Ostwald's isolation method:

This method can be used regardless of the number of reactants involved e.g., consider the reaction,

$$n_1A + n_2B + n_3C \rightarrow \text{Products}$$

This method involves obtaining the initial reaction rate with known concentrations of different reactants (such as A, B, C).

Temperature dependence of rate of a reaction:

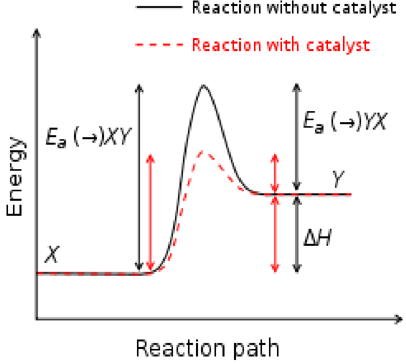
For all temperatures by 10 degrees C, the reaction rate doubles, but only 16% collisions increase. It can be defined by the Arrhenius equation.

The temperature coefficient is the rate of consistency of the reaction at two temperatures that varies by 10. The selected temperature is usually 298K and 308K.

Temperature coefficient = $R_1 + 10/R_1 \approx 2$ to 3

Activation energy (Ea):

Activation energy is defined as the minimum amount of extra energy required by a reacting molecule to get converted into product. It can also be described as the minimum amount of energy needed to activate or energize molecules or atoms so that they can undergo a chemical reaction or transformation.



Arrhenius equation:

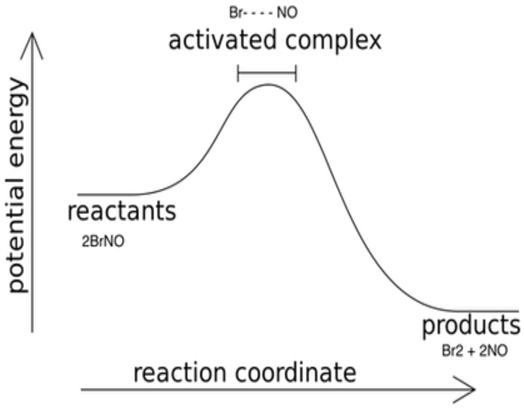
The figures were first proposed by the Dutch chemist, J.H. Van't Hoff but Swedish pharmacist, Arrhenius provided its physical justification and explanation. The equation of Arrhenius is based on Collision's theory. It is not an equation born of pure numbers we can find. It is the statistics used equal to the test data in most cases. The Arrhenius equation looks like this,

$k = A\ e^{-Ea / RT}$ .... (I)

where A is the Arrhenius factor or frequency factor. It is also known as the pre-exponential factor. This constant is straightforward in response to something. R is a stable gas and Ea is the activating factor that we measure in joules / mole.

Activated complex:

Activated Complex is a high-energy state in which reactions pass to convert reactions into products.



Q. The rate constant of a 1st order reaction increases from 3×10^{-2} to 8×10^{-2} when the temperature changes from 310K to 330K. Calculate the activation energy (Ea)?

S1. Given $k_2 = 8 \times 10^{-2}$, $k_1 = 3 \times 10^{-2}$, $T_1 = 310$ K, $T_2 = 330$K

$\text{Log}\frac{k_1}{k_2} = \frac{E_a}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\log\frac{8\times10^{-2}}{3\times10^{-2}} = \frac{E_a}{2.303R}\left(\frac{2}{310} - \frac{1}{330}\right)$

$\log 2.66 = \frac{E_a}{2.303\times8.314} \times (1.95503) \times 10^{-04}$

$0.4249 = \frac{E_a}{19.147} \times (1.95503 \times 10^{-04})$

$E_a = 41{,}613.62$ J/mole

= 41.614 kJ/mol

Q2. The rate constant of the first-order reaction raises from 3×10^{-2} to 5×10^{-2} when the temperature change from 300K to 310K. Calculate the activation energy?

S2. Given $k_2 = 3 \times 10^{-2}$, $k_1 = 5 \times 10^{-2}$, $T_1 = 300$K, $T_2 = 310$K

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

$\log\frac{5\times10^{-2}}{3\times10^{-2}} = \frac{E_a}{2.303\ R}\left(\frac{1}{300} - \frac{1}{310}\right)$

$\log 1.66 = \frac{E_a}{2.303R}(1.07526 \times 10^{-04})$

$0.2218 = \frac{E_a}{2.303\times8.314} \times (1.07526 \times 10^{04})$

$0.2218 = 5.6158 \times 10^{-6} \times E_a$

$E_a = 39{,}495.7$ J/mol

Q. The first order reaction has rate constant of 2.0×10^{-2} and 6.0×10^{-2} at 0^0C and 30^0C. Calculate the activation energy of the reaction?

S3. Given $k_2 = 6 \times 10^{-2}$, $k_1 = 2 \times 10^{-2}$, $T_1 = 273$ K, $T_2 = 303$K

$\log\frac{k_1}{k_2} = \frac{E_0}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\log\frac{6\times10^{-2}}{2\times10^{-2}} = \frac{E_a}{2.303\ R}\left(\frac{1}{273} - \frac{1}{303}\right)$

$\log 3 = \frac{E_a}{2.303R}(3.6267 \times 10^{-4})$

$0.4771 = \frac{E_a}{2.303\times8.314} \times\ (3.6267 \times 10^{-04})$

$0.4771 = 1.8941 \times 10^{-5} \times E_a$

$E_a = 25,\ 188.74$ J/mol

= 25.188 kJ/mol

Threshold energy:

Threshold Energy is the minimum amount of Kinetic Energy molecules must have in order to bring about a successful collision between two reacting molecules considered to be spheres, thus triggering a chemical reaction between these two reacting elements.

Temperature dependence of Rate of Reaction in Arrhenius Equation

In Arrhenius' calculations, the EA / RT factor corresponds to half of the molecules that defy regenerative power over Ea. Taking natural logarithms on both sides of equation I, we find,

$\ln k = -I-E_a / RT + \ln A$ .... (II)

Therefore, from the Arrhenius equation, we can find that increasing the temperature or reducing the initial energy will lead to an increase in the reaction rate and an exponential increase in the constant rate. In the power opening graph compared to the reaction rate, slope $= -E_a / R$ and break = ln A.

At room temperature T_1, equation II will be

$\ln k_1 = -I-E_a / RT_1 + \ln A$ .... (III)

At room temperature T2, equation II will be

$\ln k_2 = -E_a / RT_2 + \ln A$ .... (IV) (k_1 and k_2 are constant values in temperature T1 and T2)

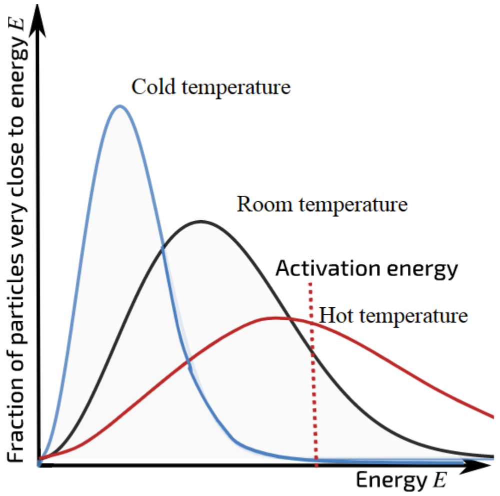
Subtracting equation III from equation IV, we find it

$\ln k_2 - \ln k_1 = E_a / RT_1 - E_a / RT_2$

$\therefore \ln k_2 / k_1 = (I\text{-}E_a / R)\ [1 / T_1 - 1 / T_2]$

$\therefore \log k_2 / k_1 = (E_a / 2.303R)\ (T_2 - T_1) / T_1T_2]$

Maxwell Boltzmann Distribution curve:



According to Maxwell and Boltzmann, the distribution of kinetic energy may be described by plotting the fraction of molecules with a given kinetic energy.

The peak of the curve corresponds to the most probable kinetic energy.

The most probable kinetic energy is the kinetic energy of maximum fraction.

When the temperature is raised, the maximum of the curve moves to the higher energy value and curve broaders out and proportion of molecules with higher energy increases.

Increasing the temperature of substance increases the fraction and molecules, which collide with energy greater than E_a.

Definition of Catalyst

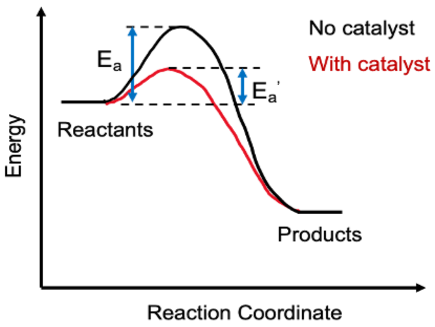
- A substance that alters the reaction rate of a particular
- chemical reaction chemically unchanged at the end of the reaction

2 Classes: I) positive catalyst
⇒ increase the rate
II) negative catalyst (inhibitor)
⇒ decrease the rate

The role of catalyst in chemical reactions:

Catalyst plays a very important role in chemical reactions. It is basically used to speed up or slow down reactions. In addition, catalyst is used to modify the chemical reaction rate. Its main functions are listed below.

A catalyst can reduce the activation of a reaction by changing the shape of the participating molecules, in order to obtain more conflict.



Collision theory:

Theory was used to predict chemical reaction rates, particularly on gases. Collision theory is based on the assumption that in order for a reaction to take place it is necessary for the reacting species (atoms or molecules) to combine or collide. However, not all conflicts bring about chemical changes. Conflict will be effective in producing chemical mutations only if the animal species are fitted with a certain amount of internal energy, equivalent to the ability to trigger a reaction. In addition, the conflicting types must be directed in a way that corresponds to the needed rearrangement of atoms and electrons. Therefore, from a contradictory point of view, the degree of chemical reaction is equal to the frequency of effective collisions. Because atomic waves or collision particles can be calculated with a certain degree of accuracy in gases only (using kinetic theory), the application of collision theory is limited to the gas phase response.

The Activated Complex theory or transition state theory:

Transition state theory (TST) defines a hypothetical “transformation” that occurs in the space between reactants and products by chemical reactions. The types formed during the transition are known as activated instruments. TST is used to describe how chemical reactions occur, and is based on the theory of conflict. Once a fixed response rate is known, TST can be used successfully to calculate normal activation enthalpy, normal activation entropy, and Gibbs normal operating power. TST is also called "activated-complex theory," "absolute-rate theory," and "complete response levels."

Photochemical Reaction:

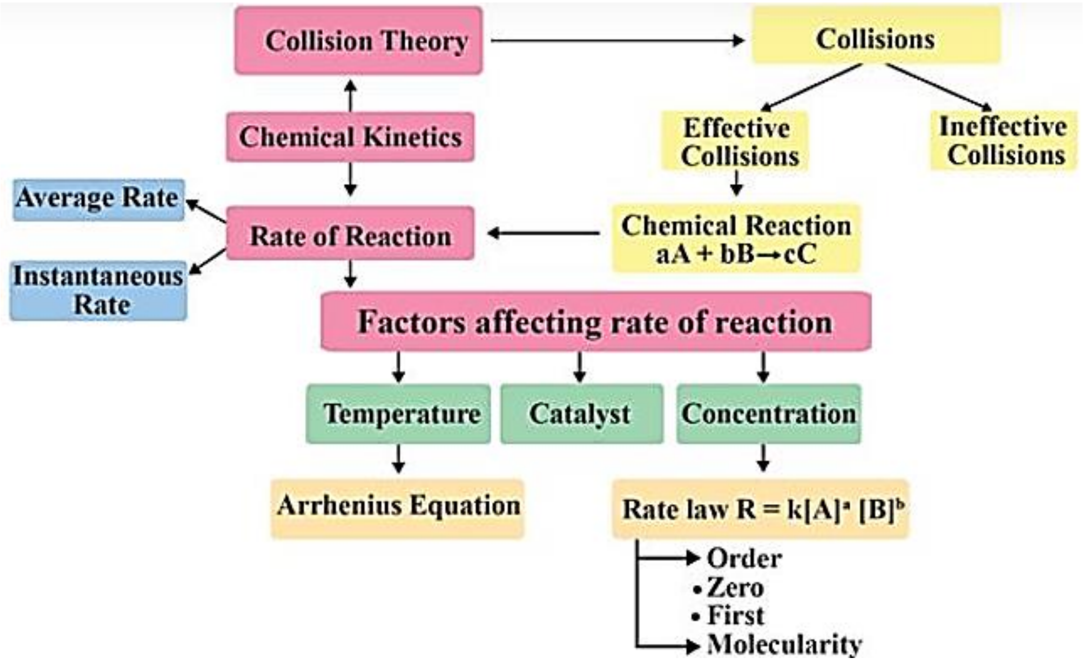
Photochemical reaction, a chemical reaction initiated by the absorption of energy in the form of light. The effect of light-absorbing molecules is the creation of temporary pleasures that have their own chemical and physical properties that are very different from the original molecules

SUMMARY

Chemical kinetics is the study of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms and formation of intermediates. The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst, affect the rate of a reaction. Mathematical representation of rate of a reaction is given by rate law. It has to be determined experimentally and cannot be predicted. Order of a reaction with respect to a reactant is the power of its concentration which appears in the rate law equation. The order of a reaction is the sum of all such powers of concentration of terms for different reactants. Rate constant is the proportionality factor in the rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation. Molecularity is defined only for an elementary reaction. Its values are limited from 1 to 3 whereas order can be 0, 1, 2, 3 or even a fraction. Molecularity and order of an elementary reaction are same.

Temperature dependence of rate constants is described by Arrhenius equation. Ea corresponds to the activation energy and is given by the energy difference between activated complex and the reactant molecules, and A (Arrhenius factor or pre-exponential factor) corresponds to the collision frequency. The equation clearly shows that increase of temperature or lowering of Ea will lead to an increase in the rate of reaction and presence of a catalyst lowers the activation energy by providing an alternate path for the reaction. According to collision theory, another factor P called steric factor which refers to the orientation of molecules which collide, is important and contributes to effective collisions, thus, modifying the Arrhenius equation to $k – PZ_{AB}e^{-Ea/RT}$

MIND MAP



MULTIPLE CHOICE QUESTIONS

1. In chemical equation $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$ the equilibrium constant Kp depends on
(a) total pressure (b) catalyst used
(c) amount of H_2 and I_2 (d) temperature

2. A reaction in which reactants (R) are converted into products (P) follows second order kinetics. If concentration of R is increased by four times, what will be the increase in the rate of formation of P?
(a) 9 times (b) 4 times
(c) 16 times (d) 8 times

3. For a reaction $x + y \rightarrow z$, rate $\propto |X|$. What is (i) molecular iiy and (ii) order of reaction?
(a) (i) 2, (ii) 1 (b) (i)2,(ii) 2
(c) (i) 1, (ii) 1 (d) (i) 1, (ii) 2

4. For a reaction $nx - y \rightarrow z$ the rate of reaction becomes twenty seven times when the concentration of X is increased three times. What is the order of the reaction?
(a) 2 (b) 1
(c) 3 (d) 0

5. The rate constant of a reaction depends upon
(a) temperature of the reaction
(b) extent of the reaction
(c) initial concentration of the reactants
(d) the time of completion of reaction

6. The unit of rate and rate constant are same for a
(a) zero order reaction
(b) first order reaction
(c) second order reaction
(d) third order reaction

7. The number of molecules of the reactants taking part in a single step of the reaction is indicative of
(a) order of a reaction
(b) molecularity of a reaction
(c) fast step of the mechanism of a reaction
(d) half-life of the reaction

8. For a unimolecular reaction
(a) the order and molecuiarity of the slowest step are equal to one
(b) molecuiarity of the reaction can be zero, one or two
(c) molecuiarity of the reaction can be determined only experimentally
(d) more than one reacting species are involved in one step

9. The overall rate of a reaction is governed by
(a) the rate of fastest intermediate'step
(b) the sum total of the rates of all intermediate steps
(c) the average of the rates of all the intermediate steps
(d) the rate of slowest intermediate step

10. The order of reaction is decided by
(a) temperature
(b) mechanism of reaction as well as relative concentration of reactants
(c) molecularity
(d) pressure

11. Rate constant in case of first order reaction is
(a) inversely proportional to the concentration units
(b) independent of concentration units
(c) directly proportional to concentration units
(d) inversely proportional to the square of concentration units

12. A first order reaction has a half-life period of 34.65 seconds. Its rate constant is
(a) $2 \times 10^{-2}\ s^{-1}$ (b) $4 \times 10^{-4}\ s^{-1}$
(c) $20\ s^{-1}$ (d) $2 \times 10^{-4}\ s^{-1}$

13· A reaction is found to be of second order with respect to concentration of carbon monoxide. If concentration of carbon monoxide is doubled, the rate of reaction will
(a) triple
(b) increase by a factor of 4
(c) double
(d) remain unchanged

14. For a chemical reaction, $X + 2Y \rightarrow Z$, if the rate of appearance of Z is 0.50 moles per litre per hour, then the rate of disappearance of Y is
(a) 0.5 mol L-1 hr-1
(b) 1.0 mol $L^{-1}min^{-1}$
(c) 0.25 mol L^{-1} hr^{-1}
(d) cannot be predicted

15. The rate of a reaction is primarily determined by the slowest step. This step is called
(a) rate determining step
(b) activation step
(c) reaction rate step
(d) none of these.

16. The reaction of high molecularity are rare because
(a) Many body collisions have a low probability.
(b) Many body collisions are not favoured energetically.
(c) Activation energy of many body collisions is very large
(d) Very high concentration is required for such reactions.

17. For a chemical reaction $A \rightarrow B$, it is found that the rate of the reaction quardruples when the concentration of A is doubled. The rate expression for the reaction is, rate = $k\,[A]^n$ where the value of n is
(a) 1 (b) 2
(c) 0 (d) 3

18. On increasing the temperature of the reacting system by 10° the rate of reaction almost becomes double. The most appropriate reason for this is that
(a) Activation energy decreases by increases of temperature
(b) The fraction of molecules having threshold energy increases
(c) Collision frequency increases
(d) The value of threshold energy decreases.

19. The half-life period of any first order reaction
(a) is half the specific rate constant
(b) is always the same irrespective of the reaction
(c) is independent of initial concentration
(d) in directly proportional to initial concentration of reactants.

20. The dimensions of rate constant of 2nd order reaction involves
(a) concentration
(b) concentration and time
(c) time only
(d) neither time nor concentration.

21. A zero order reaction A → Products, has rate constant 10^{-2} mole L^{-1} s^{-1}. If a process is started with 10 moles of A in a one litre vessel, the number of moles of reactant after 10 minutes will be
(a) 10 (b) 5
(c) 6 (d) 4.

22. For which of the following reactions, the temperature coefficient is maximum?
(a) $A \rightarrow B : E_a = 50$ kJ
(b) $P \rightarrow Q : E_a = 40$ kj
(c) $X \rightarrow Y : E_a = 60$kJ
(d) $W \rightarrow Z : E_a = 80$kJ

23. A hypothetical reaction $2p + q \rightarrow s + r$ has rate constant as 2.0×10^{-3} mol L^{-1} s^{-1}. The order of the reaction is
(a) unpredictable (b) zero
(c) one (d) two

24. The molecularity of the reaction cannot be
(a) 1 (b) 2
(c) 1.5 (d) 3.

25. For the first order reaction, the half-life is independent of
(a) catalyst
(b) temperature
(c) both catalyst and temperature
(d) initial concentration of reactants.

26. For a certain reaction aA → bB, the rate of reaction is doubled when the concentration of A is increased by four times. The rate ot reaction is equal to
(a) $k[A]^a$ (b) $k[A]^{1/2}$
(c) $k[A]^{1/a}$ (d) k[A].

27. What happens to the peak of the curve in the Maxwell-Boltzmann distribution graph if temperature increases?
(a) Shifts backward and downward
(b) Shifts forward and upward
(c) Shifts forward and downward
(d) Shifts backward and upward

28. DDT on exposure to water decomposes. Half-life = 10 years. How much time will it take for its 90% decomposition?
(a) 50 years (b) 65.5 years
(c) 500 years (d) 700 years.

29. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is
(a) 0.383 mm (b) 23.1mm
(c) 8.73 mm (d) 7.53 mm

30. The rate equation for the reaction $2A + B \rightarrow C$ is found to be: rate = k [A] [B]. The correct statement inxelation to this reaction is that the
(a) unit of R must be s-1
(b) t1/2 is constant
(c) rate of formation of C is twice the rate of disappearance of A.
(d) value of k is independent of the initial concentration of A and B.

31. The reaction $2\ SO_2\ (g) + O_2\ (g) \rightleftharpoons SO_3\ (g)$ is carried out in 1 dm^3 vessel and 2 dm^3 vessel separately. The ratio of the reaction velocities will be
(a) 1 : 8 (b) 1 : 4
(c) 4 : 1 (d) 8 : 1

32. Which of the following statements is not correct for order of a reaction?
(a) Order of a reaction can be determined experimentally.
(b) It is the sum of the powers of concentration terms in the rate law expression.
(c) It does not necessarily depend on the stoichiometric coefficients.
(d) Order of a reaction cannot be fractional.

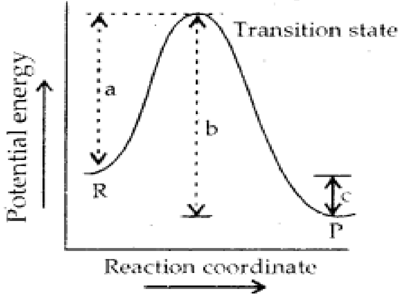
33. t1/4 can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is K, then $t_{1/4}$ can be written as
(a) 0.10/K
(b) 0.29/K
(c) 0.69/K
(d) 0.73/K

34. Collision Theory is applicable to
(a) First order reactions
(b) Zero order reactions
(c) Biomolecular reactions
(d) Intramolecular reactions.

35. The reaction A → 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?

(a) 1 hour (b) 0.5 hour
(c) 0.25 hour (d) 2 hours.

36. The potential energy diagram in the reaction R → P is given. ΔH° of the reaction corresponds to the energy.



(a) a (b) b
(c) c (d) a + b

37. 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 the reactant B is

(a) 2 (b) -1
(c) 1 (d) -2

38. The half-lives of two samples are 0.1 and 0.4 second. Their respective concentrations are 200 and 50 respectively. What is the order of the reaction?

(a) 0 (b) 2
(c) 1 (d) 4

39. When a biochemical reaction is carried out in laboratory from outside of human body in absence of enzyme, then the rate of reaction obtained is 10-6 times, then activation energy of reaction in presence of enzyme is:

(a) 6/RT
(b) P is required
(c) Different from E_a obtained in the laboratory
(d) Cannot, say anything

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

(a) C (b) l
(c) l^2 (d) Cl.

41. The rate constant of a reaction A → B is 0.6×10^3 mole per second. If the concentration of [A] is 5 M, then what will be concentration of [B] after 20 months?

(a) 0.36 M (b) 0.72 M
(c) 1.08 M (d) 3.60 M

42. A first order reaction has specific reaction rate 10^{-2} s^{-1}. How much time it will take for 20g of reactant to reduce to 5g?

(a) 138.6 s (b) 346.5 s
(c) 693.0 s (d) 238.6 s

43. The activation energy of a reaction can be determined from the slope of which of the following graph:

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

44. If cone, of reactant 'A' is increased 10 times and rate of reaction becomes 100 times. What is order with respect to 'A'?

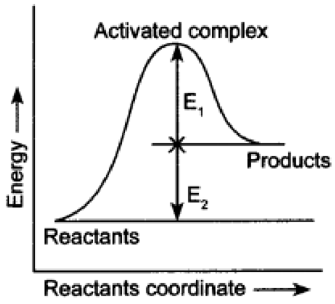
(a) 2 (b) 1
(c) 3 (d) 4

45. In the first order reaction the concentration of reactant decreases from 0.6 M to 0.3 M in 30 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M:

(a) 60 min (b) 30 min
(c) 15 min (d) 50 min

46. Consider Fig. and mark the correct option.

(a) Activation energy of forward read ion is E1 + E2 and product is less stable than reactant.
(b) Activation energy of forward reaction is E1 + E2 and product is more stable than reactant.



(c) Activation energy of both forward and backward reaction is E1 + E2 and reactant is more stable than product.
(d) Activation energy of backward reaction is E1 and product is more stable than reactant.

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

$k = A\ e^{-Ea/RT}$

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

48. Activation energy of a chemical reaction can be determined by ________ .

(a) determining the rate constant at standard temperature.
(b) determining the rate constants at two temperatures.
(c) determining probability of collision.
(d) using catalyst.

49. For a chemical reaction A→B, it is found that on increasing the concentration of A four times, the rate of the reaction doubles. the order of the reaction is

(a) two (b) a
(c) half (d) zero

50. The half-life of the first order reaction having rate constant K = 1.7 x $10^{-5}s^{-1}$ is

(a) 12.1 h (b) 9.7 h
(c) 11.3 h (d) 1.8 h

ASSERTION AND REASON

Q1. **Assertion:** The order of reaction can be zero or fractional.

Reason: The order of a reaction cannot be determined from a balanced chemical reaction.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.

Q2. **Assertion:** The order and molecularity of a reaction are always the same.

Reason: Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate-determining elementary step.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.
(e) if both are incorrect

Q3. **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.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.

Q4. **Assertion:** Instantaneous rate of reaction is equal to dx/dt

Reason: It is the rate of reaction at any particular instant of time.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.

TRUE AND FALSE

Q1. The burning of paper is exothermic because a flame is needed to start the reaction.

(a) True (b) False

Q2. In the reaction of $H_2 + O_2 \rightarrow H_2O$, an increase in activation energy will not lead to an increased rate of reaction.

(a) True (b) False

Q3. According to Le Chatelier's Principle, adding heat to the system represented by the reactants and products in the following equilibrium, $H_2 + Cl_2 <==> 2HCl$ + heat, produces more HCl.

(a) True (b) False

PRACTICE QUESTIONS (MCQ)

Q1. For the equilibrium, $A(g) \rightleftharpoons B(g)$, ΔH is −40 kJ/mol. If the ratio of the activation energies of the forward (E_f) and reverse (E_b) reactions is 2/3 then:

(a) E_f = 60kJ / mol; E_b = 100 kJ/mol
(b) E_f = 30kJ / mol; E_b = 70 kJ/mol
(c) E_f = 80kJ / mol; E_b = 120 kJ/mol
(d) E_f = 70kJ / mol; E_b = 30 kJ/mol

Q2. At 518^0 C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is :

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

Q3. For the reaction A + 2B → C, rate is given by $R = [A]\,[B]^2$ then the order of the reaction is

(a) 3 (b) 6
(c) 5 (d) 7

Q4. If 50% of a reaction occurs in 100 seconds and 75% of the reaction occurs in 200 seconds, the order of this reaction is

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

Q5. The half-life period of a first-order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301):

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

Q6. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be (R = 8.314KJmol-1 and log 2=0.301)

(a) 53.6 $KJmol^{-1}$ (b) 48.6 $KJmol^{-1}$
(c) 58.5 $KJmol^{-1}$ (d) 60.5 $KJmol^{-1}$

Q7. Decomposition of X exhibits a rate constant of 0.05 mg/year. How many years are required for the decomposition of 5 mg of X into 2.5 mg?

(a) 25 (b) 50
(c) 20 (d) 40

Q8. In a first-order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

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

Q9. The rate law for the reaction below is given by the expression k[A] [B]

A + B → Product

If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will be

(a) 3 k (b) 9 k
(c) k/3 (d) k

Q10. For the reaction, 2A + B → products, when the concentrations of A and B both were doubled the rate of the reaction increased from 0.3 mol $L^{-1}\,s^{-1}$ to 2.4 mol $L^{-1}\,s^{-1}$. When the concentration of A alone is doubled, the rate increased from 0.3 mol $L^{-1}\,s^{-1}$ to 0.6 mol $L^{-1}\,s^{-1}$. Which one of the following statements is correct?

(a) Order of the reaction with respect to B is 2.
(b) Order of the reaction with respect to B is 1.
(c) Order of the reaction with respect to A is 2.
(d) Total order of the reaction is 4.

Q11. The formation of gas at the surface of tungsten due to adsorption is the reaction of order

(a) 0 (b) 1
(c) 2 (d) insufficient data.

Q12. Higher-order (>3) reactions are rare due to:

(a) shifting of equilibrium towards reactants due to elastic collision
(b) loss of active species on collision
(c) low probability of simultaneous collision of all the reacting species
(d) increase in entropy and activation energy as more molecules are involved.

Q13. What is the rate law for acid hydrolysis of an ester such as $CH_3COOC_2H_5$ in aqueous solution?

(a) $k\,[CH_3COOC_2H_5]$
(b) $k\,[CH_3COOC_2H_5]\,[H_2O]$
(c) $k\,[CH_3COOC_2H_5]_2$
(d) k

Q14. Mechanism of a hypothetical reaction $X_2 + Y_2 \rightarrow 2 \times Y$ is given below:

(b) X + Y2 → XY + Y (slow)
(c) X + Y → XY (fast)

The overall order of reaction is

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

Q15. What is the change in the rate of a second order reaction when the concentration of the reactant is increased by 2 times its initial value?

(a) It doubles (b) No change
(c) It quadruples (d) It triples

Q16. The decomposition of N_2O_5 in CCl_4 solution was studied. $N_2O_5 \rightarrow 2NO_2 + 1/2O_2$. The rate constant of the reaction is 6.2×10^{-4} sec^{-1}. Calculate the rate when the concentration of N_2O_5 is 1.25 molar.

(a) 6.45×10^{-4} (b) 7.45×10^{-4}
(c) 6.75×10^{-4} (d) 7.75×10^{-4}

Q17. What is the formula to calculate the time taken for the completion of a zero-order reaction?

(a) $t_{100\%} = [A]_0/3k$ (b) $t_{100\%} = [A]_0/k$
(c) $t_{100\%} = [A]_0/2k$ (d) $t_{100\%} = 2[A]_0/k$

Q18. The half-life of a given reaction is doubled if the initial concentration of the reactant is doubled. What is the order of the reaction?

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

Q19. What is the time taken to complete 75 percent of the reaction if the rate of the first-order reaction is 0.023 min^{-1}?

(a) 65.97 minutes (b) 60.28 minutes
(c) 69.28 minutes (d) 50.37 minutes

Q20. For the reaction X → Y + Z, the rate constant is 0.00058 s^{-1}. What percentage of X will be decomposed in 50 minutes?

(a) 90.02 percent (b) 82.44 percent
(c) 88.82 percent (d) 82.67 percent

Q21. A first-order reaction is 50 percent complete in 30 minutes. Calculate the time taken for completion of 87.5 percent of the reaction.

(a) 30 minutes
(b) 60 minutes
(c) 90 minutes
(d) 120 minutes

Q22. Consider the following statements, The rate law for the acid catalyzed hydrolysis of an ester being given as Rate = $k[H^+][ester] = k'[acid]$. If the acid concentration is doubled at constant ester concentration

I. The second order rate constant, k is doubled
II. The pseudo first order rate constant, k is doubled
III. The rate of the reaction is doubled

Which of the above statements are correct?

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

Q23. For a reaction, $A + 2B \rightarrow C$, rate is given by $+d[C]/dt = k[A][B]$, hence, the order of reaction is

(a) I3
(b) 2
(c) I1
(d) 0

Q24. After how many seconds will the concentration of the reactants in a first order reaction be halved if the rate constant is 1.155×10^{-3} s^{-1}?

(a) I600
(b) 100
(c) I60
(d) 10

Q25. For a first order reaction, the half-life period is

(a) IDependent on the square of the initial concentration
(b) Dependent on the first power of the initial
(c) Iconcentration
(d) Dependent on the square root of initial concentration

Independent on initial concentration

Q26. For a zero order reaction, the plot of the concentration of reactant versus time is

(a) ILinear with positive slope and zero intercept
(b) Linear with negative slope and zero intercept
(c) ILinear with positive slope and non-zero intercept
(d) A curve asymptotic to concentration axis
(e) Linear with negative slope and non-zero intercept

Q27. A reaction proceeds by first order, 75% of this reaction was completed in 32 min. the time required for 50% completion is

(a) I8 min
(b) 16 min
(c) I20 min
(d) 24 min

Q28. For the reaction, $2A + B \rightarrow A_2B$, the rate law given as

(a) IK[2A][B]
(b) $K[A]^3$ [B]
(c) $IK[A][B]^3$
(d) $K[A]^2[B]$

Q29. The half-life period of a first order reaction is 69.3 s. what is the rate constant?

(a) I0.01/s
(b) 0.1/s
(c) I1/s
(d) 10/s

Q30. A reaction involving A, B, C as reactants is found to obey the rate law, rate = $k[A]^x$ $[B]^y[C]^z$. when the concentration of A, B and C are doubled separately, the rate is also found to increase two, zero and four times respectively. The overall order of the reaction is

(a) I1
(b) 2
(c) I3
(d) 4

ASSERTION AND REASON

Q1. **Assertion:** Order of the reaction can be zero or fractional.

Reason: We cannot determine order from the balanced chemical equation.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.

Q2. **Assertion:** A catalyst increases the rate of a reaction.

Reason: In presence of a catalyst, the activation energy of the reaction decreases.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.
(e) if both assertion and reason are false

Q3. **Assertion:** Activation energy of forward reaction is greater than that of backward reaction.

Reason: The reaction considered is endothermic in forward direction.

Activation energy of forward reaction is greater than that of backward reaction.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.
(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.
(c) if the assertion is the correct statement & the reason is an incorrect statement.
(d) if the assertion is incorrect statement and reason is the correct statement.
(e) if both assertion and reason are false

Q4. **Assertion:** Rate of reaction increases with increase in temperature.

Reason: Number of collision increases with increase in temperature.

(a) if both assertion & reason are correct statements and reason is the correct explanation of assertion.

(b) if both assertion & reason are correct statements and reason is not the correct explanation of assertion.

(c) if the assertion is the correct statement & the reason is an incorrect statement.

(d) if the assertion is incorrect statement and reason is the correct statement.

(e) if both assertion and reason are false.

TRUE AND FALSE

Q1. If 2.5 moles of H2 are added to 2.1 moles of CO to form CH3CH2OH, the limiting reagent is H2.

(a) True (b) False

Q2. A catalyst is formed during the transition from reactant to product.

(a) True (b) False

Q3. A factor for increasing the rate of a reaction is an increase in concentration of the reactants.

(a) True (b) False

Q4. A catalyst can alter the enthalpy ΔH of a reaction.

(a) True (b) False

SOLUTIONS MULTIPLE CHOICE

1. **(d)** For the reaction, $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$, the number of moles of gaseous reactants is equal to the number of moles of gaseous products. The equilibrium constant K_p is independent of **(a)** Total pressure
(b) Catalyst
(c) The amounts of H_2 and I_2 present
However, it changes with Temperature

2. **(c)** $R \rightarrow P$
For a second order reaction, rate $=k[R]^2$
If conc. of R is increased by four times, rate $=k[4R]^2$
Hence, the rate of formation of P increases by 16 times.

3. **(a)** Molecularity is the number of molecules that come together to react in an elementary (single-step) reaction and is equal to the sum of stoichiometric coefficients of reactants in this elementary reaction.
Two molecules, X and Y are taking part in this reaction so the molecularity of the reaction is 2.
Order of reaction is given by the rate law, power of X is 1 in the rate law, so the order of the reaction is 1.

4. **(c)** Let rate of reaction $R = k[x]^n$
$27R = k[3x]^n$ ...(ii)
Or $27 = 3^n$
[dividing (ii) by (i)]
Or $3^3 = 3^n$
Or $n = 3$

5. **(a)** The rate constant of a reaction depends upon the temperature of the reaction, i.e., rate constant (k) is constant for a particular reaction at fixed temperature.

6. **(a)**

For a zero order reaction, rate $= k[A]^0 = k$

Units $= \text{mol L}^{-1}\text{time}^{-1}$.

7. **(b)** For a single-step reaction, the molecularity of reaction is given by the sum of number of reactants that are taking part in the reaction.
For example-
$A + B \rightarrow C + D$
It is a single step reaction and total 2 molecules are taking part in the reaction, so the molecularity of reaction is 2.

8. **(a)** For a unimolecular reaction, both order and molecularity are one in the rate determining step.

9. **(d)** The reaction mechanism is the step-by-step process by which reactants actually become products. The overall reaction rate depends almost entirely on the rate of the slowest step.
If the first step is the slowest, and the entire reaction must wait for it, then it is the rate-determining step.

10. **(b)**

11. **(b)** For First order of reaction,
Rate = k [A],
$K = \frac{\text{mol/L}}{\text{sec} \times \text{mol/L}} = \text{sec}^{-1}$

12. **(a)** Order $= t_{1/2} = 34.65s$ R = ?
$t_{1/2} = \frac{0.693}{R}$
$R = \frac{0.693}{6_{1/2}}$
$K = \frac{0.693}{34.65s} = 0.025\text{-}1$
$= 2 \times 10\text{-}2 \ s\text{-}1$

13. **(b)** The rate law expression is $R=k[CO]^2$
When concentration of CO is doubled, the rate law expression becomes $R' =k[2CO]^2$
$=4k[CO]^2 = 4R$.

14. **(b)** Rate of disappearance of X -2 × rate of appearance of Z $=2 \times 0.5=0.1 \text{molL}^{-1}$.

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

16. **(a)** The reactions of higher order are rare because many body collisions have a very low probability. The chances of three or more molecules colliding at the same time to give product are very low.

17. **(b)** $\text{Rate}=k[A][B]$and $\text{Rate}=k[A]^2$ are both second order reaction. In the first case, A and B are both first order and in the second, A is second order.

If a reactant is second order, then when its concentration is doubled, the rate of the reaction quadruples ($2^2 =4$); if the concentration is tripled, the rate increases by a factor of 9 ($3^2 =9$)

18. **(c)** On increasing the temperature the kinetic energy of the reacting molecules increases and hence, number of collision increases. So that rate of reaction will also be increased.

19. **(c)** For first order reaction $T_{1/2} = 0.693/k$
So It is independent of concentration.

20. **(b)** For a second order reaction:
$K = \frac{rate}{[A]^2}$ $2A \rightarrow$ product rate $= K[A]^2$
$= \frac{Concentration}{time\ (concentration)^2}$
$= \frac{Concentration}{time\ (concentration)^2}$
$= \frac{1}{time\ concentration}$

So it involves both time & concentration. Except for first-order reactions, the unit of rate constant depends on the dimensions ($mol^{1-n}.lit^{-1}.sec^{-1}$) concentration and time.
Where n= order of the reaction.

$$k = 10^{-2}$$

$$kt = R_o - R$$

$$10^{-2} \times 10 \times 60 = \frac{10}{1} - R$$

$$R = 6\ molL^{-1}$$

6 mole react unreacted mole $= 10 - 6$

$= 4moles$

21. **(d)**

22. **(d)**

23. **(b)**

24. **(c)** Molecularity of the reaction cannot be fractional.

25. **(d)** $t_{1/2}\ of\ n^{th} order \propto \frac{1}{a^{n-1}}$
$t_{1/2} \propto \frac{1}{a^{1-1}}\ or\ t_{\frac{1}{2}} \propto \frac{1}{a^{o}}\ or\ t_{\frac{1}{2}} \propto 1$
So, for a first-order reaction, the half-life is independent of initial concentrations of reactants.

26. **(b)**

27. **(c)** Sol. With the increase of temperature, the peak shifts forward but downward. This is because with the increase of temperature, the most probable kinetic energy increases and the fraction of molecules possessing most probable kinetic energy decreases.

28. **(b)** K = $\frac{0.693}{10} yr^{-1}$
When t is 99%
$= \frac{2.303}{t} \log \frac{a}{a-0.99a} = \frac{2.303}{t} \log 10^2$
$\frac{0.693}{10} = \frac{2.303}{t_{99}} \times 2$
Or
t = $\frac{10}{0.693} \times 2.303 \times 2 = 66.5\ years$

29. **(b)** Since for a first order reactions: Rate =K[R]
Rating given = 1.5×10^{-2}M min^{-1} at 0.5 M conentration
$1.5 \times 10^{-2}Mmin^{-1}$ = K (0.5M)
K = $3 \times 10^{-2}\ min^{-1}$
Half-life = $t_{1/2}$ = 0.693/k
$t_{1/2} = \frac{0.693}{0.03\ min^{-1}}$ = 23.1 minutes

∴ Half-life of reaction is 23.1 minutes.

30. **(d)** From the rate equation rate =k[A][B], we can say that the reaction is first order in A and first order in B. Hence, the overall order of the reaction is 2.

(a) The value of k is independent of the initial concentration of A and B. Hence, the statement B is correct.

(b) The half-life period is not constant. It is inversely proportional to the concentration of reactants. Hence, the statement B is incorrect.

(c) The rate of formation of C is one half the rate of disappearance of A.
d[C]/dt = −d[A]/2dt
Hence, the statement C is incorrect.

(d) The unit of k must be $mol^{-1}s^{-1}$
Hence, the statement D is incorrect.

31. **(d)** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
For this reaction, rate
$r_1 = k[SO_3]^2\ [O_2]$
On doubling the volume of vessel, concentration would be half.
Hence, Rate (r_2) = k $\left(\frac{[SO_2]}{2}\right)^3 \left([\frac{O_2}{3}]\right) = \frac{r_\perp}{8}$
$\frac{r_1}{r_2} = 8 : 1$

32. **(d)**

33. **(b)** Let initial concentration be a_0
After concentration decreases by $\frac{1}{4} = a_0\left(1 - \frac{1}{4}\right) = \frac{3a_0}{4}$
Using first order kinetic equation,
$t_{1/4} \times k = ln\left(\frac{a_0}{3a_0/4}\right) = ln\left(\frac{4}{3}\right)$
$t_{1/4} \times \frac{0.29}{K}$

34. **(c)** Collision theory is applicable to Bi-molecular reactions and reactions with molecularity greater than two. It is not applicable to uni-molecular reactions. The basic requirement of collision theory is that the reacting species (atoms, ions or molecules) must come together and collide in order for the reaction to occur. Collisions are possible in bi-molecular reactions.

35. **(a)** $\Rightarrow k = \frac{2.303}{t} \log \frac{A_0}{At}$
Or k = $\frac{2.303}{1} \log \frac{0.8}{0.2}$ ...(i)
Remaining moles of A = 0.9 – 0.675
= 0.225
K = $\frac{2.303}{t_1} \log \frac{0.9}{0.225}$
t_1 = 1h

36. **(c)** From given figure,
Activation energy of forward reaction =a.
Activation energy of backward reaction =b.
∴△H=b−a=c

37. **(d)** Let us assume the chemical reaction:-
nA + yB ⟶ Product
Let the rate of the reaction:-
$Rate_1 = k[A]^n\ B]^y \longrightarrow a$

When the conc. of B is doubled;

Rate$_2$ = $\frac{Rate_1}{4} = k[A]^n[2B]^y \rightarrow b$

Now divide equation a by b:–

4 = $\frac{1}{2y}$

$\Rightarrow 2^2 = \frac{1}{2y} or \Rightarrow 2^y = \frac{1}{2^2}$

⇒y=−2 with respect to B

Hence the correct answer is option A=−2

i.e., the order of the reaction with respect to reactant B is −2

38. **(b)** $t_{\frac{1}{2}} = \frac{1}{a^{n-1}}$

Where a is the initial amount and n is the order

$\frac{(t_{1/2})_2}{(t_{1/2})_2} = \frac{(a^{n-1})_2}{(a^{n-1})_1}$

$\frac{0.1}{0.8} = \left[\frac{50}{400}\right]^{n-1}$

$\frac{1}{8} = \left[\frac{1}{8}\right]^{n-1}$

$8^{-1} = 8^{-1}(n-1)$

-1 = - n + 1

N = 2

39. **(c)** When a biochemical reaction is carried out laboratory from outside of human body in absence of enzyme, then rate of reaction obtain 10^6 times than activation energy of reaction presence of enzyme. It is different from E_a^0b in laboratory because for a given chemical reac $k=Ae^{-Ea/RT}$ (Arrhenius equation)

40. **(b)** In photo initiated primary process, rate of reaction is directly proportional to intensity of light uses.

41. **(b)** Rate = $\frac{[R]_0-[R]}{t}$

$\Rightarrow 0.6 \times 10^{-3} \times 20 \times 60 = [R]_0 - [R]$

⇒ 0.72 M

Amount of [B] produced = $[R]_0$–[R]

= 0.72M

42. **(a)** $t_{3/4} = \frac{1.386}{k} = \frac{1.386}{10^2} = 138.6\ s$

43. **(a)** When we plot Ink Vs 1/T

slope of line = $-E_a/R$

44. **(a)** $\vartheta_{old} = k[A]^n$; $\vartheta_{new} = k\ [10A]^n$

$\frac{\vartheta_{new}}{\vartheta_{old}} = 100 = 10^n$

N =2

45. **(a)** t3/4= 2t1/2 = 2 × 30 = 60 min.

46. **(a)** $E_a = E_1 + E_2$ and products are less stable due to higher energy.

47. **(d)** Rate constant (k) increases exponentially by decreasing activation energy and increasing temperature because lesser the activation energy and temperature, more will be rate of reaction and rate constant ‘k’

48. **(b)** $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

By knowing k_x at T, and k_2 at T_2, we can determine E_a (activation energy)

49. **(c)** R = $[K]^m$

Also 2r = $K[4A]^m$

$\left[\text{Thus} \frac{1}{2} = \left(\frac{1}{4}\right)^m\right.$

$\therefore m = \frac{1}{2}$

50. **(c)** K $1.7 \times 10^{-5}\ s^{-1}$

$l_{1/3} = \frac{0.693}{k} = \frac{0.639}{1.7\times10}$

= 11.3h

ASSERTION AND REASON

1. **(b)** The assertion is correct as the order can be zero or fraction but it can be determined experimentally.

2. **(e)** Order and molecularity can be same only for elementary reaction and it is different for complex reaction.

Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate-determining elementary step.

3. **(b)** For a zero order reaction, $t_{1/2} = [A_0]/2K$.

As half-life for zero order reaction is directly proportional to initial concentration, hence doubling the concentration of reactant, half-life get doubled.

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

TRUE AND FALSE

1. **(b)** Burning paper is exothermic because the reaction releases heat.

2. **(a)** (It will lead to a decrease in reaction rate).

3. **(b)** Adding heat will shift the equilibrium to the left thus decreasing HCl production.

PRACTICE SOLUTIONS

1. **(c)** $A(g) \rightarrow B(g)$
Given $\Delta H = -40 KJ/mol$
$E_f / E_b = 2/3$
$\therefore E_f = 2/3 \, E_b$
$\Delta H = E_b - E_f$
$-40 = E_b - 2/3 \, E_b$
$-40 = 1/3 \, E_b$
$\therefore E_b = -40 \times 3 = -120$ KJ/mol
$E_f = E_b - \Delta H$
$= -120 - (-40)$
$= -120 + 40$
$= -80$ KJ/mol

S2. **(d)** $r_1 = 1$ torr/sec
When 5% is reacted, 95% is unreacted.
$r_2 = 0.5$ torr/sec
When 33% is reacted, (67% is unreacted)
m = order of reaction,
unreacted = a-x
$r_1/r_2 = [(a-x_1)/(a-x_2)]^m$
$1/0.5 = (0.95/0.67)^m$
$2 = (1.414)^m$
$\Rightarrow 2 = \sqrt{2}^m$
$\Rightarrow m = 2$
So order of the reaction is 2

S3. **(a)** The order of the reaction is the sum of the power of the concentration terms in rate law expression.
$R = [A] [B]_2$
So, order of reaction = 1+2 = 3

S4. **(a)** $t_{1/2} = 100$ second (50% reaction)
After 200 seconds, 75% of reaction will be completed,
i.e., $t_{75\%} = 200$ seconds.
So, it follows first-order kinetics as the half-life is independent of concentration and follows the relation $t_{3/4} = 2 \times t_{1/2}$

S5. **(a)** Given half-life period $t_{1/2} = 6.93$ min.
Decay constant, $\lambda = 0.693/ t_{1/2}$
$= 0.693/ 6.93$
$= 0.1$ /min
Let t be time required for completion of chemical reaction.
We have $t = (2.303/ \lambda) \log (a/a-x)$
$\therefore t = (2.303/0.1) \log (100/100-99)$
$\therefore t = (2.303/0.1) \log 100$
$\therefore t = (2.303/0.1) \times 2$
$t = 46.06$ min

S6. **(a)** $\ln k_2/k_1 = -(E_a/2.303R)(1/T_2 - 1/T_1)$
$r_2/r_1 = k_2/k_1 = 2$
Given $T_1 = 300K$
$T_2 = 310$ K
$\log(2) = -(E_a/2.303 \times 8.314) [(1/310) - (1/300)]$
$0.301 = -E_a/19.147 [(300-310)/93000]$
$0.301 = -E_a/19.147 [-10/93000]$
$E_a = 0.301 \times 19.147 \times 9300$
$= 53598.19$ J
$= 53.6$ kJ/mol

7. **(b)** According to unit of rate constant it is a zero-order reaction.
$t_{1/2} = a_0 / 2k$
$= 5/2 \times 0.05$
$= 50$ years

8. **(a)** Gine that the concentration of the reactant decreases from 0.8 M to 0.4 M in 15 minutes.
$t_{1/2} = 15$ minute.
So, the concentration of reactant will fall from 0.1 M to 0.025 M in two half-lives.
i.e., $2t_{1/2} = 2 \times 15 = 30$ minutes.

9. **(d)** The rate constant varies with the temperature only. It is independent of the concentration of reactants. So the rate constant will be k.

10. **(a)** If concentration of [A] is doubled, then the rate will be doubled, so the order of A is 1.
Then again if the concentration of A and B both were doubled, the rate will increase 8 times. Rate $= [2A] [2B]^2 = 8[A] [B]^2$
So the order of B is two.
So, the overall order is 3.

11. **(a)** Adsorption on the metal surface do not depend on the concentration of gas.
So it is a zero-order reaction.

12. **(c)** Higher-order (>3) reactions are rare due to the low probability of simultaneous collision of all the reacting species.

13. **(a)** We know that the acid hydrolysis of ester can be expressed as $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$
Sometimes, if the reactant is used excessively compared to the other. The order of the reaction can be altered or even controlled.
According to the rate law, Rate = k [A] × [B] y
$= k [CH_3COOC_2H_5] [H_2O]$
But as the water is excessive, it will be R= k $[CH_3COOC_2H_5]$.

14. **(c)**

15. **(c)** Suppose the initial concentration of reactant is [A]
Hence, as mentioned in the question, the concentration of reactant = 2 × [A]
As per the second order reaction rate, it will be = $k \times [A]^2$
According to this equation the rate for 2 × [A] = $k \times 4 \times [A]^2$

Finally from this equation, we can conclude that, when the concentration of the reactant is doubled in a second order chemical kinetics reaction, the reaction rate will be quadruples.

16. **(d)** Given,
$N_2O_5 \rightarrow 2NO_2 + 1/2\ O_2$
Rate = $k[N_2O_5]^1$
Rate =$6.25 \times 10^{-4} \times [1.25]$
Rate = 7.75×10^{-4}.

17. **(b)** The time taken for the zero-order reaction to complete can be calculated as follows:
When the reaction is complete, $[A]_0 = 0$
Therefore, $k = [A]_0/t$ or $t_{100\%} = [A]_0/k$.

18. **(b)** Half-life ($t_{1/2}$) is the time required for a quantity to reduce to half of its initial value. The half-life of a zero-order reaction is directly proportional to its initial concentration. They are related as:
$t_{1/2} = [R]_0/2k$.

19. **(b)** Given, the reaction is 75 complete so, a=75
Rate of the reaction k=0.023 min^{-1}
First-order integrated rate equation, k = 2.303/t(log100/100−a)
t=2.303/0.023(log100/100−75) = 60.28 minutes.

20. **(b)** Given, rate constant k= 0.00058 s^{-1}
Time t= 50 minutes = 50 × 60 = 3000 seconds
First-order integrated rate equation, k = 2.303/t(log100/100−a)
log100/100−a = kt/2.303
log100/100−a = 0.00058×3000/2.303 = 0.756
a=82.44 percent.

21. **(c)** Reaction is 50 percent complete in 30 minutes. Hence, $t_{1/2}$ = 30 minutes
75 percent of the reaction is completed in two half-lives. Hence, t = 2 × 30 = 60 minutes
87.5 percent of the reaction is completed in three half-lives. Hence, t = 3 × 30 = 90 minutes.

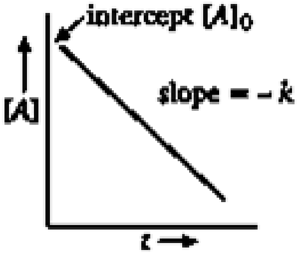
22. **(b)** Pseudo first order rate constant is doubled as well as rate of reaction is doubled. It may be noted that in presence of acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of k depends upon the concentration of H^+ ions, otherwise rate constant of a reaction is constant at constant temperature.

23. **(b)** Rate of the reaction depends upon the concentration of A and B both, hence it is a second-order reaction

24. **(a)** $t_{1/2} = 0.693/k$
$4 = 0.693/1.155 \times 10^{-3}$
0.6×10^3
= 600

25. **(d)** $T_{1/2}$ of n^{th} order $\propto \frac{1}{a^{n-1}}$
$t_{1/2} \propto \frac{1}{a^{1-l}}\ or \propto \frac{1}{a^0}\ or\ t_{1/2} \propto 1$
So, for a first-order reaction, the half-life is independent of initial concentrations of reactants.

26. **(e)** For a zero order reaction, the plot of concentration of reactant vs time is a straight line (linear) with a negative slope and non-zero intercept.



27. **(b)** For first order areaction
$K = \frac{2.303}{t} \log 10 \frac{a}{(a-x)}$
where, a = initial concentration
x = change in concentration during time ‘t’.
If 75% of the reaction was completed in 32 min, then
$K = \frac{2.303}{32} \log 10 \frac{100}{(100-75)}$
$= \frac{2.303}{32} \log_{10}4$
K = 0.0433 min^{-1}
Hence, time required for the completion of 50% reaction
$T = \frac{2.303}{0.0433} \log_{10}2$
= 16 min

28. **(d)** For the reaction $2A + B \rightarrow A_2B$
According to rate law,
Rate is directly proportional to concentration of reactants
Rate = $k[A]^2[B]$

29. **(a)** First order rkt $t_{1/2}$ = 69.3
$\Rightarrow \frac{ln2}{k} = 69.3$
$\Rightarrow k = \frac{ln}{69.3} = \frac{0.693}{69.3}$
= 10^{-2}
∴ r = k[R]
= $10^{-2} \times 10^{-1}$
= 10^{-3-}M/s

30. **(c)** On doubling the concentration of A, the rate of reaction becomes two times.
The order of reaction w.r.t. A is 1.
On doubling the concentration of B, the rate of reaction does not change.
The order of reaction with respect to B is 0.
On doubling the concentration of C, the rate of reaction becomes four times.
The order of reaction with respect to C is 2.
The overall order of reaction =1+0+2=3

ASSERTION AND REASON

1. **(b)** The assertion is correct as the order can be zero or fraction but it can be determined experimentally.

2. **(e)** A catalyst may increase on decrease the rate of reaction. In the presence of a catalyst, the activation energy of the reaction increases.

3. **(a)** Endothermic reactions absorb energy to proceed in forward reaction. Therefore activation energy is more for the forward reaction.

4. **(b)** Rate of reaction increases with increase in temperature. On increase of temperature number of collisions increases. But the increase in the rate of reaction with increase in temperature is mainly due to increase in the number of effective collisions.

TRUE AND FALSE

1. **(b)** this reaction is flawed in class we discussed this and agreed to change the product to $C_2H_6O_2$; first, get the balanced equation. $2 CO + 3H_2$ $C_2H_6O_2$; OK now assume that H2 is limiting. Then solve for the moles of CO needed to react with it: #mol CO needed = 2.5 mol H2 (2 mol CO/3 mol H_2)=5/3 mol CO=2.67 mol CO needed. But this is less than the 2.1 mol CO we have so in fact, CO is limiting.

2. **(b)** It is present before and after a reaction. In a sense it is both a reactant and a product.

3. **(a)**

4. **(b)**.