Very Short Answer Questions (PYQ)

Q.1. Express the rate of following reaction in terms of disappearance of hydrogen in the reaction

 $3H_2(g) + N_2(g)
ightarrow 2NH_3(g)$

[CBSE (AI) 2007]

Ans.

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

Rate of disappearance of $H_2=-rac{d/H_2/}{dt}=-3rac{d/N_2/}{dt}=rac{3}{2}rac{d/\,\mathrm{NH_3}\,/}{dt}$

Q.2. Define 'order of a reaction'.

[CBSE (AI) 2011]

Ans. Order of a reaction may be defined as the sum of the powers of the concentration terms of the reactants in the rate law expression.

Q.3. The equation $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{e}$ has zero order. What is the rate equation?

[CBSE (AI) 2005]

Ans. Rate = $k[A]^0 [B]^0$ or Rate = k.

Q.4. For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction?

[CBSE Delhi 2006]

Ans.

Let the rate law for the reaction be

 $r = k [A]^n \qquad \dots (i)$

According to the question,

$$27r = k[3A]^n \qquad \dots (ii)$$

Dividing equation (ii) by equation (i), we get

$$\frac{27r}{r} = \frac{k/3A/^n}{k/A/^n}$$

or $3^3 = 3^n$ \therefore n = 3

$$r = k [A]^3$$
 \therefore Order of reaction, $n = 3$.

Q.5. In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why?

[CBSE Delhi 2013]

Ans. This is due to improper orientation of the colliding molecules at the time of collision.

Q.6. Identify the order of reaction from the following unit for its rate constant: L $mol^{-1}s^{-1}$

[CBSE (F) 2010]

Ans. Second order.

Q.7. For a reaction $\mathbf{R} \rightarrow \mathbf{P}$, half-life $(\mathbf{t}_{1/2})$ is observed to be independent of the initial concentration of reactants. What is the order of reaction?

[CBSE (AI) 2005]

Ans. First order.

Q.8. Define 'activation energy' of a reaction.

[CBSE (AI) 2011]

Ans. The energy required to form the intermediate called activated complex is known as activation energy. Activation energy = Threshold energy – Average energy of the reactants

Q. 9. What is the effect of adding a catalyst on

Q. Activation energy (Ea), and

Ans. Decreases

Q. Gibbs energy (ΔG) of a reaction?

[CBSE (AI) 2017]

Ans. No effect

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Very Short Answer Questions (OIQ)
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Q. 1. What do you understand by 'Rate of reaction'?

Ans. The change in the concentration of any one of the reactants or products per unit time is termed as the rate of reaction.

Q.2. When does the average rate of reaction become equal to instantaneous rate?

Ans. Average rate becomes equal to instantaneous rate when the interval, Δt , approaches zero, *i.e.*, it becomes infinitesimally small. Thus,

 r_{inst} i.e., $\left(\frac{\mathrm{dx}}{\mathrm{dt}}\right) = \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t}$.

Q.3. Why is it that instantaneous **r**ate of **r**eaction **d**oes not change when a pa**r**t of the **r**eacting solution is taken out?

Ans. Instantaneous rate is measured over a very small interval of time, hence, it does not change when a part of solution is taken out.

Q.4. For the assumed reaction $X_2+3Y_2\rightarrow 2XY_3$, write the rate of equation in terms of rate of disappearance of Y_2 .

[HOTS]

Ans.

Rate = $-\frac{d/X_2}{dt}$ = $-\frac{1}{3}\frac{d/Y_2}{dt}$ = $+\frac{1}{2}\frac{d/XY_3}{dt}$

Rate of disappearance of $Y_2 = -\frac{d/Y_2}{dt} = -3\frac{d/X_2}{dt} = +\frac{3}{2}\frac{d/XY_3}{dt}$

Q.5. Give an example of a pseudo first order reaction.

Ans.

Acid catalysed hydrolysis of ethyl acetate:

 $CH_3COOC_2H_5 + H_2O \xrightarrow{\mu^+} CH_3COOH + C_2H_5OH$ Rate = $k[CH_3COOC_2H_5]$

Q.6. For which type of reactions, order and molecularity have the same value?

[NCERT Exemplar]

Ans. If the reaction is an elementary reaction, order is same as molecularity.

Q.7. For a reaction, $A + B \rightarrow Product$, the rate law is given by $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

[NCERT Exemplar]

Ans.

Order of reaction = $\frac{1}{2} + 2 = \frac{5}{2}$

Q.8. State a condition under which a bimolecular reaction is kinetically first order.

[NCERT Exemplar]

Ans. A bimolecular reaction may become kinetically of first order if one of the reactants is in excess.

Q.9. What is the difference between rate law and law of mass action?

Ans. Rate law is an experimental law. On the other hand, law of mass action is a theoretical law based on the balanced chemical reaction.

Q.10. Define specific reaction rate or rate constant.

Ans. Specific reaction rate is the rate of reaction when the molar concentration of each of the reactants is unity.

Q.11. For the reaction $A \rightarrow B$, the rate of reaction becomes three times when the concentration of **A** is increased by nine times. What is the order of reaction?

[HOTS]

Ans.

Let, $r = k [A]^n$...(*i*)

Given,

...(*ii*)

Dividing equation (ii) by (i), we get

 $3r = k [9A]^n$

	${3r\over r} = {k/9A/^n\over k/A/^n}$ =	$\frac{9^n k/A/^n}{k/A/^n}$	
	$3 = 9^{n}$	or	$3^1 = 3^{2n}$
⇒	2n = 1	or	$n = \frac{1}{2}$

Rate, $r = k[A]^{1/2}$ л.

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

Q.12. Following graph is a plot of the rate of a reaction vs concentration of the reactant. What is the order of the reaction?

[HOTS]



Ans. Zero order reaction, as the rate of reaction is independent of concentration of reactant.

Q.13. For a reaction, A + B \rightarrow Products, the rate law is – Rate = $k[A][B]^{3/2}$

Can the reaction be an elementary reaction? Explain.

[HOTS]

Ans. During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with respect to B would have been 1, but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not an elementary reaction.

Q.14. A reaction is 50% complete in **2** hours and 75% complete in 4 hours. What is the order of the reaction?

[HOTS]

Ans. As *t*_{75%} = 2*t*_{50%}

Therefore, it is a first order reaction.

Q.15. Why does the rate of a reaction increase with rise in temperature?

[NCERT Exemplar]

Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.*, the activation energy), which leads to faster rate.

Q.16. Why is the probability of reaction with molecularity higher than three very rare?

[NCERT Exemplar]

Ans. The probability of more than three molecules colliding simultaneously is very small. Hence, possibility of molecularity being three is very low.

Q.17. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example.

[NCERT Exemplar]

Ans. Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.

Q.18. Can a reaction have zero activation energy?

[HOTS]

Ans. If $E_a = 0$, then according to Arrhenius equation $k = Ae^{-E_a/RT} = Ae^0 = A$. This implies that every collision results into a chemical reaction which cannot be true. Hence, a reaction cannot have zero activation energy.

Q.19. Define threshold energy of a reaction.

Ans. Threshold energy is the minimum energy which must be possessed by reacting molecules in order to undergo effective collision which leads to formation of product molecules.

Short Answer Questions-I (PYQ)

Q.1. Define the following:

Elementary step in a reaction

Ans. Elementary step: The reaction which takes place in a single step is called an elementary reaction. For example,

 $N_2(g) + O_2(g) \rightarrow 2NO(g)$

Q.2. Rate of reaction

[CBSE (AI) 2009; (F) 2010]

Ans. Rate of **r**eaction: The rate of reaction may be defined as the decrease in concentration of reactant or increase in concentration of product per unit time.

For a hypothetical reaction, $R \rightarrow P$

Rate of reaction =
$$\frac{-\Delta/R}{\Delta t} = \frac{+\Delta/P}{\Delta t}$$

Q. Write two differences between 'order of reaction' and 'molecularity of reaction'.

[CBSE Delhi 2014]

Ans. Differences between order and molecularity of reaction:

S.No	Order	M olecula r ity
(<i>i</i>)	It is the sum of the powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously so as to result into a chemical reaction.
(<i>ii</i>)	It is determined experimentally.	It is a theoretical concept.
(<i>iii</i>)	It can be zero or a fraction.	It cannot be zero or a fraction.
(<i>iv</i>)	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning.

Q. 3.

For a reaction: $2NH_3(g) \xrightarrow{P_1} N_2(g) + 3H_2(g)$

Rate = k

- i. Write the order and molecularity of this reaction.
- ii. Write the unit of k.

[CBSE South 2016]

Ans.

- i. Zero order, bimolecular
- ii. mol L⁻¹ s⁻¹

Q.4. Define the following terms:

Q. Pseudo first order reaction

Ans. A reaction which is not truly of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, *e.g.*, acid hydrolysis of ethyl acetate.

 $CH_{3}COOC_{2}H_{5} + H_{2}O \rightarrow H+ CH_{3}COOH + C_{2}H_{5}OH$

Rate \propto [CH₃COOC₂H₅] as H₂O is in excess.

Q. Half life period of reaction (t_{1/2})

[CBSE Delhi 2014]

Ans. The half life $(t_{1/2})$ of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration $[R]_0$.

For a first order reaction, $t_{1/2} = \frac{0.693}{k}$, *i.e.*, independent of $[R]_0$.

For a zero order reaction, $t_{1/2} = \frac{/R_0}{2k}$, *i.e.*, $t_{1/2} \propto [R]_0$.

Q.5. Answer the following questions:

Q.

For a reaction $A + B \rightarrow P$, the rate law is given by,

$$r = k[A]^{1/2}[B]^2.$$

What is the order of this reaction?

Ans.

Order of reaction = $\frac{1}{2} + 2 = \frac{5}{2}$

Q. A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half life of the reaction.

[CBSE (AI) 2013]

Ans.

Radioactive decay follows first order kinetics.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}}$$
 s = 1.26 × 10¹³ s

Q.6. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction?

[CBSE (AI) 2011]

Ans. Consider the reaction $nR \rightarrow$ Products

As the reaction is of second order

:...Rate,
$$r = k [R]^2$$
 ...(*i*)

If the concentration of the reactant reduced to half, then

Rate,
$$t' = k \left[\frac{R}{2}\right]^2 \qquad \dots (ii)$$

Dividing equation (ii) by (i), we get

$$\frac{r'}{r} = \frac{k / R/^2}{4k / R/^2} = \frac{1}{4}$$

 $r' = \frac{1}{4}r$, *i.e.*, rate of reaction becomes $\frac{1}{4^{\text{th}}}$ of the initial rate.

The unit of rate constant is **mol**⁻¹ L s⁻¹.

Q. 7. Answer the following questions:

Q. Explain why H₂ and O₂ do not react at room temperature.

Ans. Due to high activation energy for the reaction.

Q. Write the rate equation for the reaction $A_2+3B_2\rightarrow 2C$, if the overall order of the reaction is zero.

[CBSE (AI) 2017]

Ans. Rate = $k[A_2]^0[B_2]^0$ or Rate = k

Q.8. Show that in a first order reaction, time required for completion of 99.9% is 10 times that of half-life $(t_{1/2})$ of the reaction.

[CBSE (F) 2016]

Ans.

$$egin{aligned} t &= rac{2.303}{k} \log rac{/R/_0}{/R/} \ &rac{t_{99.9\%}}{t_{50\%}} &= rac{rac{2.303}{k} \log rac{100}{100 - 99.9}}{rac{2.303}{k} \log rac{100}{100 - 50}} &= rac{\log rac{100}{\log rac{100}{50}} \ &= rac{\log 10^3}{\log 2} &= rac{3 \log 10}{0.3010} \ &rac{t_{99.9\%}}{t_{50\%}} &= rac{30}{3.01} \simeq 10 \ &t_{99.9\%} &= 10t_{50\%} \end{aligned}$$

Q.9. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs. time (t) plot is given as



- i. Predict the order of the reaction.
- ii. What is the slope of the curve?

[CBSE (AI) 2014]

Ans.

i. Order of the reaction is zero.

ii. Slope = $\frac{d/R}{dt} = -k$

Q.10. What **d**o you un**d**erstan**d** by the rate law an**d** rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are:

[CBSE (AI) 2011]

- i. L⁻¹ mol s⁻¹
- ii. L mol⁻¹ s⁻¹.

Ans. An experimentally determined expression which relates the rate of reaction with the concentration of reactants is called rate law while the rate of reaction when concentration of each reactant is unity in a rate law expression is called rate constant.

Comparing power of mole in L^{-1} mol s^{-1} and (mol L^{-1})¹⁻ⁿ s^{-1} , We get

 $1 = I - n \Rightarrow n = 0$ *i.e.*, zero order reaction

Again comparing power of mole in L mol⁻¹s⁻¹ and (molL-1)1-ns-1, we get

 $-1 = 1 - n \Rightarrow n = 2$, *i.e.*, second order reaction

Q.11. The rate constant for a first order reaction is 60 s⁻¹. How much time will it take to reduce the initial concentration of the reactant to $\frac{1}{10}$ th of its initial value?

[CBSE (F) 2013]

Ans.

$$t = rac{2.303}{k} \log rac{/R_{l_0}}{/R_l}$$
 as $[R] = rac{/R_{l_0}}{10}$
 $\therefore \quad t = rac{2.303}{k} \log rac{/R_{l_0}}{rac{/R_{l_0}}{10}} = rac{2.303}{60} imes \log 10 = rac{2.303}{60} imes 1 = 3.838 imes 10^{-2} s$

Q.12. The rate constant for a zero order reaction is 0.0030 mol L^{-1} s⁻¹. How long will it take for the initial concentration of the reactant to fall from 0.10 **M** to 0.075 **M**?

[CBSE (F) 2010]

Ans.

Given: $[R_0] = 0.10 \text{ M}$ [R] = 0.075 M

$$k = 0.0030 \text{ mol } L^{-1} \text{ s}^{-1}, t = ?$$

We know that
$$k = \frac{|R_0| - |R|}{t}$$

or

$$t=rac{|R_0|-|R|}{k}=rac{0.10-0.075}{0.0030}=8.33~s.$$

Short Answer Questions-I (OIQ)

Q.1. Why does the rate of any reaction generally decrease during the course of the reaction?

[NCERT Exemplar]

Ans. The rate of reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate of reaction decreases.

Q.2. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

[NCERT Exemplar]

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined

by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

Q.3. For a zero order reaction will the molecularity be equal to zero? Explain.

[NCERT Exemplar]

Ans. No, the molecularity can never be equal to zero or a fractional number. Molecularity is the number of molecules involved in each elementary reaction which may be different, *i.e.*, the molecularity of each step may be different.

Q.4. Differentiate between rate of reaction and reaction rate constant.

Ans.

S. No.	Rate of Reaction	Reaction Rate Constant
(<i>i</i>)	Rate of reaction is the change in concentration of a reactant or product in a unit interval of time.	It is the rate of reaction when the molar concentration of each of the reactants is unity.
(<i>ii</i>)	The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time.	The rate constant does not depend upon the concentrations of the reactants.
(<i>iii</i>)	Its units are always mol litre ⁻¹ time ⁻¹ .	Its units depend upon the order of reaction.

Q.5. The form of the rate law for a reaction is expressed as: rate = $k[Cl_2][NO]^2$

Find out the orders of the reaction with respect to Cl₂ and with respect to NO and also the overall order of this reaction.

Ans. Order with respect to $CI_2 = 1$, Order with respect to NO = 2,

Overall order = 1 + 2 = 3

Q.6. Calculate the overall order of a reaction which has the rate expression,

i. Rate =
$$k[A]^{1/2} [B]^{3/2}$$

Ans.

i. Order = $\frac{1}{2}$ + $\frac{3}{2}$ = 2, *i.e.*, second order. ii. Order = $\frac{3}{2}$ + (-1) = $\frac{1}{2}$, *i.e.*, half order. Q.7. For a reaction: $A + H_2O \rightarrow B$, Rate $\propto [A]$.

What is its (i) molecularity (ii) order of reaction?

Ans.

- i. Pseudo unimolecular
- ii. Order = 1.

Q.8. Answer the following questions:

Q. The conversion of the molecule X to Y follows second order kinetics. If the concentration X is increased to three times, how will it affect the rate of formation of Y?

Ans.

Rate = $k [X]^2$	
$r_1 = k \left[X \right]^2$	(<i>i</i>)
$r_2 = k \left[3X \right]^2$	(<i>ii</i>)

Dividing (ii) by (i),

$$\frac{r_2}{r_1} = \frac{9k \ /X/^2}{k \ /X/^2}$$
 or $r_2 = 9r_1$

Thus, rate of formation of Y will increase by nine times.

Q. The specific reaction rate of a reaction is 6.2×10^{-3} mol L⁻¹ s⁻¹. What is the order of reaction?

Ans. Comparing the unit of k, with the general unit (mol L^{-1})¹⁻ⁿ s⁻¹, we get

$$mol^{1-n} = mol^1$$

 \Rightarrow *n* = 0, *i.e.*, zero order reaction.

Q.9. The rate law for the reaction: Ester + $H^+ \rightarrow Acid$ + Alcohol is:

$$\frac{\mathrm{dx}}{\mathrm{dt}} = k \left[\text{Ester} \right] \left[\mathrm{H}^{+} \right]^{0}$$

What would be the effect on the rate if (*i*) concentration of the ester is doubled? (*ii*) concentration of H⁺ is doubled?

Ans. (i) The rate of reaction will be doubled. (ii) No effect on rate.

Q.10. Derive an expression to calculate time required for completion of zero order reaction.

[NCERT Exemplar]

Ans.

$$t = \frac{/R/_0 - /R/}{k}$$

For completion, [R] = 0

$$\therefore$$
 $t = \frac{/R_0}{k}$

Q.11. The rate constant for a reaction of zero order in A is 0.0030 mol L⁻¹ s⁻¹. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

Ans.

⇒

$$k = 0.0030 \text{ mol } \text{L}^{-1}\text{s}^{-1}$$
, $[R]_0 = 0.10 \text{ M}$, $[R] = 0.075 \text{ M}$

We know that

$$[R] = -kt + [R]_0$$

0.075 = -0.0030t + 0.10

 $3t = 100 - 75 \implies t = 8.33$ seconds

Q.12. The following data were obtained during the first order thermal decomposition of SO₂Cl₂ at a constant volume:

$$SO_2Cl_2(\boldsymbol{g}) \rightarrow SO_2(\boldsymbol{g}) + Cl_2(\boldsymbol{g})$$

Expe r iment	Time/secon d -1	Total p r essu r e/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: $\log 4 = 0.6021$, $\log 2 = 0.3010$)

[HOTS]

Ans.

$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

Here, $P_0 = 0.4$ atm, t = 100 s, $P_t = 0.7$ atm

λ.

$$k = \frac{2.303}{100} \log \frac{0.4}{2 \times 0.4 - 0.7}$$
$$= \frac{2.303}{100} \log \frac{0.4}{0.1} = \frac{2.303}{100} \log 4 = \frac{2.303}{100} \times 0.6021$$
$$k = 1.386 \times 10^{-2} \text{ s}^{-1}$$

Q.13. 87.5% of the substance **d**isinteg**r**ate**d** in 45 minutes (fi**r**st o**rder r**eaction). What is its half-life?

Ans.

$$\left(\frac{1}{2}\right)^n = \frac{12.5}{100}$$
 because 87.5% has disintegrated, amount left is 12.5%.

 $\left(\frac{1}{2}
ight)^n = \left(\frac{1}{8}
ight) \qquad \Rightarrow \qquad \left(\frac{1}{2}
ight)^n = \left(\frac{1}{2}
ight)^3$

Number of half lives = 3

 $t_{1/2} = \frac{45}{3} = 15$ minutes

Q.14. The rate for the reaction $R \rightarrow P$ is rate = k[R]. It has been shown graphically below. What is rate constant for the reaction?





From the graph

Case I: Rate = k[A]1 × 10⁻² mol L⁻¹ s⁻¹ = k (0.1 mol L⁻¹)

A

$$k = \frac{1 \times 10^{-2} \text{ mol } L^{-1} s^{-1}}{0.1 \text{ mol } L^{-1}} = 0.1 \text{ s}^{-1}$$

Case II:

 $3 \times 10^{-2} \text{ mol } \mathrm{L}^{-1} \mathrm{s}^{-1} = k (0.3 \text{ mol } \mathrm{L}^{-1})$

$$k = \frac{3 \times 10^{-2} \text{ mol } L^{-1} s^{-1}}{0.3 \text{ mol } L^{-1}} = 0.1 \text{ s}^{-1}$$

Hence, $k = 0.1 \text{ s}^{-1}$

Q.15. Answer the following questions on the basis of the given plot of potential energy vs reaction coordinate:

- i. What is the threshold energy for the reaction?
- ii. What is the activation energy for forward reaction?
- iii. What is the activation energy for backward reaction?
- iv. What is enthalpy change for the forward reaction?



Ans.

- i. Threshold energy for the reaction = 300 kJ mol^{-1}
- ii. Activation energy for the forward reaction = 300 150

$$= 150 \text{ kJ mol}^{-1}$$

- iii. Activation energy for the backward reaction = 300 100
 - $= 200 \text{ kJ mol}^{-1}$
- iv. Enthalpy change for the forward reaction $\Delta_r H = 100 150$

 $= -50 \text{ kJ mol}^{-1}$

Q.16. A graph between $\ln \mathbf{k}$ and $\frac{1}{T}$ for a reaction is given. Here \mathbf{k} is rate constant and \mathbf{T} is temperature in Kelvin.

[HOTS]

If **OA** = **a** and **OB** = **b**, answe**r** the following:

- i. What is the activation energy (*E*_a) of the reaction?
- ii. What is the frequency factor (A) for the reaction?



Ans.

According to Arrhenius equation, $\ln k = - rac{\mathrm{E}_a}{\mathrm{RT}} + \ln A$

i. Slope =
$$-\frac{OB}{OA} = -\frac{b}{a} = -\frac{E_a}{R}$$
 or $E_a = \frac{b}{a}R$

ii. Intercept on y-axis = $OB = b = \ln A$ or $A = e^{b}$

Q.17. Rate constant **k** for first order reaction has been found to be 2.54×10^{-3} s⁻¹. Calculate its three-fourth life.

[CBSE Sample Paper 2013]

Ans.

$$t=rac{2.303}{k}\lograc{/R_{
m /o}}{/R/}$$
 ... (i) $k=2.54 imes10^{-3}s^{-1}; [R]=rac{/R_{
m /o}}{4}$

Substituting these values in equation (i), we get

$$t_{3/4} = \frac{2.303}{2.54 \times 10^{-3}} \log \frac{\frac{R_{0}}{4}}{\frac{R_{0}}{4}} = 0.9066 \times 10^{3} \log 4$$
$$t_{3/4} = 0.9066 \times 10^{3} \times 0.6021 \text{ s} = 5.46 \times 10^{2} \text{ s}$$

Q.18. After 24 hrs, only 0.125 gm out of the initial quantity of 1 gm of a radioactive isotope remains behind. What is its half life period?

[CBSE Sample Paper 2017]

Ans.

Here, $[R]_0 = 1$ g, [R] = 0.125 g, t = 24 h

$$k = rac{2.303}{t} \log rac{/R/_0}{/R/}
onumber \ k = rac{2.303}{24} \log rac{1}{0.125}$$

$$egin{aligned} &k = rac{2.303}{24} \log 8 \ &k = rac{2.303}{24} imes 0.9031 \ &k = 0.0866 \ h^{-1} \ &t_{1/2} = rac{0.693}{k} \ &t_{1/2} = rac{0.693}{0.0866 \ h^{-1}} \ & ext{or} \ &t_{1/2} = 8 \ h \end{aligned}$$

Q.19. A first order gas reaction $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $K = 2.0 \times 10^{-4} \text{ s}^{-1}$. What percentage of A_2B_2 is decomposed on heating for 900 seconds.

[CBSE Sample Paper 2013]

Ans.

$$k = \frac{2.303}{t} \log \frac{/R_{b}}{/R/}$$

$$2.0 \times 10^{-4} s^{-1} = \frac{2.303}{900} \log \frac{/R_{b}}{/R/}$$

$$\log \frac{/R_{b}}{/R/} = \frac{2.0 \times 10^{-4} \times 900}{2.303} = 0.0781$$

$$\log \frac{/R/}{/R_{b}} = -0.0781$$

$$\frac{/R/}{/R_{b}} = \text{Antilog } \overline{1.9219}$$

$$\frac{/R/}{/R_{b}} = 0.835$$

 $[R] = 0.835 [R]_0$ If $[R]_0 = 100$, then

[*R*] = 83.5

R]₀ – [R] = 100 – 83.5 = 16.5, *i.e.*, 16.5% of initial concentration has changed into products.

Q.20. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.

 $2H_2O_2 \stackrel{\text{\tiny OH}^-}{\to} 2H_2O + O_2$

This reaction takes place in two steps as given below:

Step-I $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)

Step-II $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ (fast)

i. Write the rate law expression and determine the order of reaction w.r.t. H_2O_2 .

ii. What is the molecularity of each individual step?

Ans.

i. Rate = $k [H_2O_2]^1 [I^-]^1$ Order of reaction w.r.t $H_2O_2 = 1$

ii. Molecularity of step I = 2 and step II = 2.

Short Answer Questions-II (PYQ)

Q. Define half-life of a reaction. Write the expression of half-life for

[CBSE (F) 2014]

- i. zero order reaction and
- ii. first order reaction.

Ans. The half life $(t_{1/2})$ of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

i. $t_{1/2}$ for a zero order reaction = $\frac{/R_{0}}{2k}$ where $[R]_{0}$ = initial concentration, k = rate constant ii. $t_{1/2}$ for a first order reaction = $\frac{0.693}{k}$

Q.5. The reaction, $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0 × 10⁻⁵. Suppose in a case $[N_2] = 0.80$ mol L⁻¹and $[O_2] = 0.20$ mol L⁻¹ before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K.

[CBSE (AI) 2012] [HOTS]

Ans.

	N2	+ O ₂ –	→ 2NO
Initial conc. in mol L ⁻¹	0.8	0.2	0
Change in conc. in mol L ⁻¹	- <i>x</i>	- <i>x</i>	+2 <i>x</i>
Equilibrium conc. in mol L ⁻¹	0.8– <i>x</i>	0.2– <i>x</i>	2 <i>x</i>

$$K_C = rac{/ ext{ NO }/^2}{/N_2/ \ /O_2/}$$
 \therefore $1 \ imes \ 10^{-5} \ = \ rac{(2x)^2}{(0.8 - x) \ (0.2 - x)}$

As $x \ll 0.2$, therefore $0.8 - x \approx 0.8$ and $0.2 - x \approx 0.2$

 $\therefore 1 \times 10^{-5} = \frac{4x^2}{0.16} \implies 4x^2 = 16 \times 10^{-7}$ $x = 6.324 \times 10^{-4} \text{ mol } \text{L}^{-1}$

Thus at equilibrium,

 $[NO] = 2x = 2 \times 6.324 \times 10^{-4}$ $= 12.648 \times 10^{-4} \text{ mol } \text{L}^{-1}$ $[N_2] = 0.8 - 6.324 \times 10^{-4} \text{ mol } \text{L}^{-1}$ $= 0.799 \text{ mol } \text{L}^{-1}$ $[O_2] = 0.2 - 6.324 \times 10^{-4} \text{ mol } \text{L}^{-1}$ $= 0.199 \text{ mol } \text{L}^{-1}$

Q.3. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

 $\log k = 14.2 - \frac{1.0 \times 10^4}{T}$ K

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.

(Given: $\mathbf{R} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

[CBSE Delhi 2016]

Ans.

Comparing the equation, $\log k = 14.2 - \frac{1.0 \times 10^4}{T}$ K with the equation, $\log k = \log A - \frac{E_a}{2.303 \text{ RT}}$, we get

$$\frac{E_a}{2.303 \text{ RT}} = \frac{1.0 \times 10^4 \text{ K}}{T} \text{ or } E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times \text{R}$$
$$E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1}$$
$$= 19.1471 \times 10^4 \text{ J} \text{ mol}^{-1}$$
$$= 191.47 \text{ kJ mol}^{-1}$$

For a first order reaction, $t_{1/2} = \frac{0.693}{k}$ or $k = \frac{0.693}{t_{1/2}}$

$$\therefore k = \frac{0.693}{200 \text{ min}} = 3.465 \times 10^{-3} \text{ min}^{-1}$$

Q.4. Following data are obtained for the reaction:

 $N_2O_5 \rightarrow 2 \operatorname{NO}_2 + \frac{1}{2}O_2$

t/s	0	300	600
[N₂O₅]/mol L⁻¹	1.6×10 ^{−2}	0.8×10 ⁻²	0.4×10 ⁻²

- i. Show that it follows first order reaction.
- ii. Calculate the half-life.

(D)

(Given log 2 = 0.3010, log 4 = 0.6021)

[CBSE Delhi 2017]

Ans.

i. At 300 s,

$$\begin{split} k &= \frac{2.303}{t} \log \frac{/R_{0}}{/R/} \\ &= \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303}{300} \log 2 \\ k &= \frac{2.303}{300} \times 0.3010 = 2.31 \times 10^{-3} s^{-1} \\ \text{At 600 s} \\ k &= \frac{2.303}{t} \log \frac{/R_{0}}{/R/} \\ &= \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303}{600} \log 4 \\ k &= \frac{2.303}{600} \times 0.6021 = 2.31 \times 10^{-3} s^{-1} \end{split}$$

k is constant and is equal to $2.31 \times 10^{-3} \text{ s}^{-1}$ when we use first order equation. Hence, it follows first order reaction.

ii.
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.31 \times 10^{-3} s^{-1}} = 300 s$$

Q.5. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (*E*_a).

 $(\log 2 = 0.301, \log 3 = 0.4771, \log 4 = 0.6021)$

[CBSE Patna 2015]

Ans.

Substituting $k_1 = 2 \times 10^{-2}$, $k_2 = 4 \times 10^{-2}$, $T_1 = 300$ K, $T_2 = 310$ K, R = 8.314 J K^{-1} mol⁻¹ in the expression

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$
$$\log \frac{4 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314} \left(\frac{310 - 300}{300 \times 310}\right)$$
$$\log 2 = \frac{E_a}{19.147} \times \frac{10}{300 \times 310}$$
$$E_a = 0.3010 \times 19.147 \times 300 \times 31 = 53598 \text{ J mol}^{-1}$$
$$E_a = 53.598 \text{ kJ mol}^{-1}$$

Short Answer Questions-II (OIQ)

Q.1. $A + 2B \rightarrow 3C + 2D$. The rate of disappearance of **B** is 1×10^{-2} mol L⁻¹ s⁻¹. What will be

- i. Rate of the **r**eaction
- ii. Rate of change in concentration of A and C?

Ans.

i. As
$$\frac{-d/B}{dt} = 1 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

 \therefore Rate $= -\frac{1}{2} \frac{d/B}{dt} = \frac{1}{2} \times 1 \times 10^{-2} = 0.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$
ii. Rate $= -\frac{d/A}{dt} = -\frac{1}{2} \frac{d/B}{dt} = +\frac{1}{3} \frac{d/C}{dt}$

Rate of change in concentration of A

$$= - \frac{d /A}{dt} = - \frac{1}{2} \frac{d /B}{dt}$$
$$= 0.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

Rate of change in concentration of C

$$= + \frac{d /C}{dt} = - \frac{3}{2} \frac{d /B}{dt} = \frac{3}{2} \times 1 \times 10^{-2}$$
$$= 1.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

Q.2. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide.

[HOTS]

$$2 \operatorname{NO}(g) + O_2(g) \rightarrow 2 \operatorname{NO}_2(g)$$

The rate law for this reaction is:

Rate =
$$k [NO]^2 [O_2]$$

Propose a mechanism for the reaction.

Ans.

The probable proposed mechanism may be,

$$NO + O_2 \rightarrow NO_3$$
 (fast) Step I

$$\mathrm{NO}_3$$
 + NO $\stackrel{_{h_1}}{\rightarrow}$ NO_2 + NO_2 (slow) Step II

Since slowest reaction is the rate determining step, therefore

Rate =
$$k_1 [NO_3] [NO]$$

$$K = \frac{/NO_3/}{/NO//O_2/}$$

$$[NO_3] = K [NO] [O_2]$$

Rate = $k_1 K [NO] [O_2] [NO] = K [NO]^2 [O_2]$, where $K = k_1 . K$

Q.3. The rate of reaction, $2NO+Cl_2 \rightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes eight times when concentration of both NO and Cl_2 are doubled. Deduce the order of the reaction.

[HOTS]

Ans. Let
$$r = k [NO]^{x} [Cl_2]^{y}$$
 ...(i)

$$2r = k [NO]^{x} [2Cl_2]^{y}$$
 ...(ii)

$$8r = k [2NO]^{x} [2Cl_2]^{y}$$
 ...(iii)

Dividing (iii) by (ii), we get

$$\frac{8r}{2r} = \frac{k / 2 \text{ NO } / x / 2 \text{ Cl}_2 / y}{k / \text{ NO } / x / 2 \text{ Cl}_2 / y}$$
$$2^2 = [2]^x$$
$$x = 2$$

Putting the value of x in (i) and (ii), we get

$$r = k [NO]^{2} [Cl_{2}]^{y}$$

$$2r = k [NO]^{2} [2Cl_{2}]^{y}$$

$$\frac{2r}{r} = \frac{/2 Cl_{2} / y}{/ Cl_{2} / y}$$

$$2 = [2]^{y}$$

$$y = 1$$
Rate = k [NO]^{2} [Cl_{2}]^{1}

Overall order of reaction = x + y = 2 + 1 = 3

Q.4. A solution of H_2O_2 when titrated against KMnO₄ solution at different intervals of time gave the following results:

Time (minutes)	0	10	2 0
Volume of K M nO4 (mL)	2 3.8	14.7	9.1

Show that decomposition of H₂O₂ is first order reaction.

Ans.

i. $k = \frac{2.303}{10} \log \frac{23.8}{14.7} = \frac{2.303}{10} \times 0.2093 = 0.048 \text{ min}^{-1}$ ii. $k = \frac{2.303}{20} \log \frac{23.8}{9.1} = \frac{2.303}{20} \times 0.4176 = 0.048 \text{ min}^{-1}$

Since the value of *k* comes out to be constant in both the cases, therefore the reaction is of first order.

Q.5. Following reaction takes place in one step:

 $2 \operatorname{NO}(g) + O_2(g) \rightarrow 2 \operatorname{NO}_2(g)$

How will the rate of the above reaction change if the volume of the reaction vessel is reduced to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume?

[HOTS]

Ans.

Rate = $k [NO]^2 [O_2]$

Let initially, moles of NO = a, moles of O₂ = b, volume of the vessel = V. Then

$$[NO] = \frac{a}{V}M, [O_2] = \frac{b}{V}M$$

a,

Rate
$$(r_1) = k \left(\frac{a}{V}\right)^2 \left(\frac{b}{V}\right) = k \frac{a^2 b}{V^3}$$
 ...(i)

Now, new volume = $\frac{V}{3}$

 \therefore New concentrations: [NO] = $\frac{a}{V/3} = \frac{3a}{V}$

$$\left[O_2\right] = \frac{b}{V/3} = \frac{3b}{V}$$

$$\therefore \qquad \text{New rate } (r_2) = k \left(\frac{3a}{V}\right)^2 \left(\frac{3b}{V}\right) = \frac{27 \, \text{ka}^2 \, b}{V^3} \qquad \dots (\text{ii})$$

λ.

 $\frac{r_2}{r_1} = 27$ or $r_2 = 27r_1$, *i.e.*, rate becomes **27 times.**

Thus, there is no effect on the order of reaction.

Q.6. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at a constant volume:

 $2N_2O_5(\boldsymbol{g}) \rightarrow 2N_2O_4(\boldsymbol{g}) + O_2(\boldsymbol{g})$

S. No.	Time/s	Total P r essu r e/atm
1.	0	0.5
2.	100	0.51 2

Calculate the rate constant.

[HOTS]

Ans. Let the pressure of $N_2O_5(g)$ decrease by 2*x* atm. As two moles of N_2O_5 decompose to give two moles of $N_2O_4(g)$ and one mole of $O_2(g)$, the pressure of $N_2O_4(g)$ increases by 2*x* atm and that of $O_2(g)$ increases by *x* atm.

$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$				
At $t = 0$	0.5 atm 0 atm 0 atm			
At time t	(0.5 – 2 <i>x</i>) atm	2 <i>x</i> atm	xatm	

 $p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

 $x = p_t - 0.5$

 $p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$

= (0.5 - 2x) + 2x + x = 0.5 + x

 $x = p_t - 0.5$

 $p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$

At t = 100 s; $p_t = 0.512$ atm,

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476$$
 atm

Thus, $k = \frac{2.303}{t} \log \frac{p_i}{p_A}$ = $\frac{2.303}{100 \ s} \log \frac{0.5 \ \text{atm}}{0.476 \ \text{atm}}$ = $\frac{2.303}{100 \ s} \times 0.0216 = 4.98 \times 10^{-4} \ s^{-1}$

Q.7. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $\mathbf{k} = 1.6 \times 10^6 \text{ s}^{-1}$ at **2**80 K? [$\mathbf{R} = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$]

Ans.

Given
$$T_1 = 280$$
 K, $k_1 = 1.6 \times 10^6$ s⁻¹, $k_2 = ?$, $E_a = 0$, $T_2 = 300$ K.

By Arrhenius equation,

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

As, $E_a = 0$

 $\therefore \qquad \log \frac{k_2}{k_1} = 0$

or

$$\frac{k_2}{k_1} = 1$$
 or $k_2 = k_1$

Thus, the rate constant at 300 K is $1.6 \times 10^6 \text{ s}^{-1}$.

Q.8. The rate constant for the decomposition of ethyl iodide

$$C_2H_5I(\boldsymbol{g}) \rightarrow C_2H_4(\boldsymbol{g}) + HI(\boldsymbol{g})$$

at 600 K is 1.60×10^{-5} s⁻¹. Its energy of activation is **2**09 kJ/mol. Calculate the rate constant of the reaction at 700 K.

Ans. We know that,

$$\log k_{2} - \log k_{1} = \frac{E_{a}}{2.303 \ R} \left[\frac{1}{T_{1}} - \frac{1}{T_{2}} \right]$$

$$\log k_{2} = \log k_{1} + \frac{E_{a}}{2.303 \ R} \left[\frac{1}{T_{1}} - \frac{1}{T_{2}} \right]$$

$$\log k_{2} = \log \left(1.60 \times 10^{-5} \text{ s} \right) + \frac{209000 \ J \ \text{mol}^{-1}}{2.303 \times 8.314 \ J \ \text{mol}^{-1} \ K^{-1}} \left[\frac{1}{600 \ K} - \frac{1}{700 \ K} \right]$$

$$\log k_{2} = -4.796 + 2.599 = -2.197 \text{ or } k_{2} = \text{Antilog} \left(\overline{3}.803 \right)$$

$$k_{2} = \mathbf{6.36} \times \mathbf{10^{-3} \ s^{-1}}$$

Q.9. A certain reaction is 50% complete in **2**0 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

$$[\mathbf{R} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; \log 4 = 0.602]$$

[HOTS]

Ans.

For a first order reaction,
$$k = \frac{0.693}{t_{1/2}}$$

 $T_1 = 300 \text{ K},$
 $k_1 = \frac{0.693}{20} = 3.456 \times 10^{-2} \text{ min}^{-1}$
 $T_2 = 350 \text{ K},$
 $k_2 = \frac{0.693}{5} = 1.386 \times 10^{-1} \text{ min}^{-1}$
 $\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1}\right]$
 $\log \frac{1.386 \times 10^{-1}}{3.465 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314} \left(\frac{350 - 300}{350 \times 300}\right)$
 $\log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{50}{350 \times 300}\right)$

$$0.602 = \frac{E_a}{19.147} \left(\frac{50}{350 \times 300}\right)$$
$$E_a = \frac{0.602 \times 19.147 \times 350 \times 300}{50}$$
$$= 24205.63 \text{ J mol}^{-1} = 24.206 \text{ kJ mol}^{-1}$$

Q.10.

 $^{238}_{92}U$ changes to $^{206}_{92}Pb$ by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb had accumulated due to decay of ^{238}U , find out the age of the ore. (Half-life of $^{238}U = 4.5 \times 10^9$ years)

[HOTS]

Ans.

 $[A]_{0} = \text{Initial amount of } {}^{238}\text{U} = \text{amount of } {}^{238}\text{U} \text{ left at time } t + \text{amount of } {}^{238}\text{U} \text{ decayed}$ $[A]_{0} = 1.0 + \text{amount of } {}^{238}\text{U} \text{ decayed} = \frac{0.1 \times 238}{206} \text{ g} = 0.1155 \text{ g}$ $\therefore [A]_{0} = 1.0 \text{ g} + 0.1155 \text{ g} = 1.1155 \text{ g}$ $\text{Determination of } k: k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^{9}} = 0.154 \times 10^{-9} \text{ year}^{-1}$ $\text{Determination of time: } t = \frac{2.303}{k} \log \frac{|A|_{0}}{|A|}$ $\text{Substituting the values of } [A]_{0} = 1.1155 \text{ g} \text{ and } k = 0.154 \times 10^{-9} \text{ year}^{-1}$ $t = \frac{2.303}{0.154 \times 10^{-9}} \log \frac{1.1155}{1}$ $= 0.7099 \times 10^{9} \text{ year}$ $= 7.099 \times 10^{8} \text{ year}$

Q.11. Observe the graph in diagram and answer the following questions.

[CBSE Sample Paper 2017]



- If slope is equal to $-2.0 \times 10^{-6} \text{ sec}^{-1}$, what will be the value of rate constant? How does the half-life of zero order reaction relate to its rate constant? i.
- ii.

Ans.

i. Slope
$$= -\frac{k}{2.303}$$
 or $k = -2.303 \times \text{Slope}$
 $\therefore \qquad k = -2.303 \times (-2.0 \times 10^{-6} \text{ s}^{-1})$
 $k = 4.606 \times 10^{-6} \text{ s}^{-1}$

ii. For a zero order reaction

$$t = rac{/R/_0 - /R/}{k}$$

At $t = t_{1/2}, [R] = rac{/R/_0}{2}$
 $\therefore \quad t_{1/2} = rac{/R/_0 - rac{/R/_0}{2}}{k} \quad ext{or} \quad t_{1/2} = rac{/R/_0}{2k}$

Long Answer Questions (PYQ)

Q.1. For the reaction,

$2 \operatorname{NO}(g) + \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{NOCl}(g),$

the following data were collected. All the measurements were taken at 263 K:

Expe r iment	Initial [NO] (M)	Initial [Cl2] (M)	Initial r ate of d isappea r ance of Cl² (M /min)
1	0.15	0.15	0.60
2	0.15	0.30	1. 2 0
3	0.30	0.15	2 .40
4	0. 2 5	0. 2 5	?

i. Write the expression for rate law.

ii. Calculate the value of **r**ate constant an**d** specify its units.

iii. What is the initial rate of disappearance of Cl₂ in experiment 4?

[CBSE Delhi 2012]

Ans. Suppose order w.r.t. NO is m and order w.r.t. Cl₂ is n. Then the rate will be

Rate =
$$k [NO]^m [Cl_2]^n$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$0.60 = k(0.15)^m (0.15)^n \qquad \dots (i)$$

$$1.20 = k(0.15)^m (0.30)^n \dots$$
(ii)

$$2.40 = k(0.30)^m (0.15)^n \qquad \dots (iii)$$

Dividing equation (iii) by (i), we get

 $\frac{2.40}{0.60} = \frac{k \ (0.30)^m \ (0.15)^n}{k \ (0.15)^m (0.15)^n}$

$$4 = 2^m$$
 or $22 = 2^m$ or $m = 2$

Dividing equation (ii) by (i), we get

$$\frac{1.20}{0.60} = \frac{k \ (0.15)^m \ (0.30)^n}{k \ (0.15)^m \ (0.15)^n}$$
$$2 = 2^n \text{ or } n = 1$$

i. Rate law expression is, Rate = $k[NO]^2 [Cl_2]$ ii. 0.60 mol L⁻¹ min⁻¹ = $k(0.15 \text{ mol } L^{-1})^2 (0.15 \text{ mol } L^{-1})$ $k = 177.77 \text{ mol}^{-2} L^2 \text{ min}^{-1}$ iii. Rate = 177.77 mol⁻² L² min⁻¹ × (0.25 mol L⁻¹)² (0.25 mol L⁻¹)

 $= 2.778 \text{ mol } L^{-1} \text{ min}^{-1}$

Q.2. Answer the following questions:

Q. For a reaction $A + B \rightarrow P$, the rate is given by

Rate = **k**[**A**] [**B**]²

- a. How is the rate of reaction affected if the concentration of B is doubled?
- b. What is the overall order of reaction if A is present in large excess?

Ans. (a) Rate, $r = k [A] [B]^2$

If concentration of *B* is doubled, then

 $r' = k [A] [2B]^2$

 $r' = 4k [A] [B]^2$, *i.e.*, the **r**ate will inc**r**ease by 4 times.

(b) As A is present in large excess therefore, order of the reaction w.r.t. A will be zero.

Rate = $k [A]^0 [B]^2 = k [B]^2$

: Order of reaction = 2

Q. A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010)

[CBSE Delhi 2015]

Ans.

 $t_{1/2} = 30 \text{ min.}$ $[R] = [R]_0 - 90\% \text{ of } [R]_0 = [R]_0 - \frac{90 / R/_0}{100}$ $[R] = \frac{/R/_0}{10}$ $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$ $t = \frac{2.303}{k} \log \frac{/R/_0}{/R/}$ $t = \frac{2.303}{0.0231} \log \frac{/R/_0}{\frac{/R/_0}{10}} = \frac{2.303}{0.0231} \log 10$ t = 99.7 min.

Q.3. Nitrogen pentoxide decomposes according to equation:

$$2N_2O_5(\textbf{g}) \rightarrow 4NO_2(\textbf{g}) + O_2(\textbf{g})$$

This first order reaction was allowed to proceed at 40°C and the data below were collected:

[N ₂ O ₅] (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

i. Calculate the rate constant. Include units with your answer.

ii. What will be the concentration of N₂O₅ after 100 minutes?

iii. Calculate the initial rate of reaction.

[CBSE Delhi 2011]

Ans. i. When t = 20 min, $[R] = 0.289 \text{ mol } L^{-1}$

Also, $[R]0 = 0.400 \text{ mol } L^{-1}$

For a first order reaction

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

$$k = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

$$k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$k = \frac{2.303}{20} / \log 4.00 - \log 2.89/$$

$$k = \frac{2.303}{20} / 0.6021 - 0.4609/$$

$$k = \frac{2.303}{20} \times 0.1412$$

$$k = 2.303 \times 0.00706 = 0.016259 \text{ min}^{-1}$$

$$k = 1.6259 \times 10^{-2} \text{ min}^{-1}$$

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

ii.
$$t = \frac{2.303}{k} \log (1 + 1)^{1/2}$$

Here, $[R]_0 = 0.400 \text{ mol}^{-1}$, t = 100 min, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

$$100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{|R|}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{|R|} \implies 0.7060 = \log \frac{0.4}{|R|}$$
Antilog (0.7060) = $\frac{0.4}{|R|}$

$$5.082 = \frac{0.4}{|R|} \implies [R] = \frac{0.4}{5.082} = 0.0787 M$$

iii. Initial rate, *i.e.*, rate of reaction when t = 0

When,
$$t = 0.00 \text{ min}, [R] = 0.400 \text{ mol } L^{-1}$$

Also, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

 \therefore Initial rate = k [R]

= $1.626 \times 10^{-2} \text{ min}^{-1} \times 0.400 \text{ mol } \text{L}^{-1}$

 $= 6.504 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$

Q.4. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	30	60
[CH ₃ COOCH ₃]/mol L ⁻¹	0.60	0.30	0.15

- i. Show that it follows pseudo first order reaction, as the concentration of water remains constant.
- ii. Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(Given $\log 2 = 0.3010$, $\log 4 = 0.6021$)

[CBSE Delhi 2015]

Ans.

i.
$$k = \frac{2.303}{t} \log \frac{/R_0}{/R}$$
 ...(*i*)

Substituting $[R]_0 = 0.60 \text{ mol } L^{-1}$, $[R] = 0.30 \text{ mol } L^{-1}$ and t = 30 s in equation (*i*), we get

 $k = \frac{2.303}{30} \log \frac{0.60}{0.30}$ $k = \frac{2.303}{30} \log 2 = \frac{2.303}{30} \times 0.3010 \qquad k = 0.0231 \text{ s}^{-1}$

Again substituting, $[R]_0 = 0.60 \text{ mol } L^{-1}$, $[R] = 0.15 \text{ mol } L^{-1}$ and t = 60 in equation (*i*), we get

 $k = \frac{2.303}{60} \log \frac{0.60}{0.15}$ $k = \frac{2.303}{60} \times \log 4 = \frac{2.303}{60} \times 0.6021 \qquad k = 0.0231 \text{ s}^{-1}$

As the value of k is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.

ii. Average rate =
$$-\frac{\Delta / CH_3 COOCH_3 /}{\Delta t}$$

= $\frac{-/0.15 - 0.30 /}{60 - 30} = \frac{0.15}{30}$

Average rate = $0.005 \text{ mol } \text{L}^{-1} \text{ s}^{-1}$

Q.5. Answer the following questions:

Q. A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

[CBSE (F) 2017]

Ans.

For a first order reaction, $t = rac{2.303}{k} \log rac{/R/_0}{/R/}$

$$\therefore \qquad \frac{t_{3/4}}{t_{1/2}} = \frac{\frac{2.303}{k} \log \frac{100}{25}}{\frac{2.303}{k} \log \frac{100}{50}} = \frac{\log 4}{\log 2} = \frac{0.6021}{0.3010}$$

Q.



where $[\mathbf{R}]_0$ is the concentration of reactant.

(Given: $\log 2 = 0.3010$, $\log 4 = 0.6021$)

Ans. (a) First order (b) Zero order

Long Answer Questions (OIQ)

Q.1. Consider the reaction $R \xrightarrow{k} P$. The change in concentration of **R** with time is shown in the following plot:

[HOTS]

- i. Predict the order of the reaction.
- ii. Derive the expression for the time required for the completion of the reaction.
- iii. What does the slope of the above line indicate?



Ans.

- i. The reaction R
 ightarrow P is a zero order reaction.
- ii. For the reaction $R \stackrel{*}{
 ightarrow} P$

rate = $\frac{-d/R}{dt} = k$

$$d\left[R\right] = -k \, dt$$

Integrating both sides,

[R] = -kt + C, where $C = \text{constant of integration} \dots (i)$

At t = 0, $[R] = [R]_0$

Substituting this in equation (i)

$$C = [R]_0$$

Substituting the value of C in equation (i)

$$[R] = -kt + [R]_0 \qquad \dots (ii)$$

$$kt = [R]_0 - [R]$$

$$\Rightarrow t = \frac{/R_0 - /R}{k}$$

On completion of reactions, [R] = 0

$$\therefore t = rac{/R_0}{k}$$

iii. From equation (ii), we have slope of curve

Slope =
$$\frac{d / R}{dt} = -k$$

Q.2. Answer the following questions:

Q. For an elementary reaction

$$\mathbf{2}A + B \rightarrow 3C$$

the rate of appearance of C at time 't' is 1.3×10^{-4} mol L⁻¹ s⁻¹.

Calculate at this time

- a. rate of the reaction.
- b. rate of disappearance of A.

Ans.

a. Rate =
$$\frac{1}{3} \frac{d/C}{dt}$$

= $\frac{1}{3} \times 1.3 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1} = 0.43 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$
b. Rate = $\frac{-d/A}{dt}$ = $\frac{2}{3} \times \frac{d/C}{dt}$
= $\frac{2}{3} \times 1.3 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1} = 0.86 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$

Q. The decomposition of N₂O₅(g) is a first order reaction with a rate constant of 5 × 10⁻⁴ s⁻¹ at 45°C, *i.e.*, 2N₂O₅(g) \rightarrow 4NO₂(g) + O₂(g). If initial concentration of N₂O₅ is 0.25 **M**, calculate its concentration after 2 min. Also, calculate half-life for decomposition of N₂O₅(g).

Ans.

$$[R]_0 = 0.25$$
 M, $t = 2$ min $= 2 \times 60$ s $= 120$ s, $k = 5.0 \times 10^{-4}$ s⁻¹

For a first order reaction,

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

$$5.0 \times 10^{-4} = \frac{2.303}{120} \log \frac{0.25}{|R|} \text{ or } \log \frac{0.25}{|R|} = 0.026$$

$$\log \frac{|R|}{0.25} = -0.026 \text{ or } \frac{|R|}{0.25} = \text{Antilog (1.974)}$$

$$\frac{|R|}{0.25} = 0.9419 \text{ or } [R] = 0.235 \text{ m}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5 \times 10^{-4} s^{-1}} = 1386 \text{ s}$$

Q.3. For a certain chemical reaction variation in the concentration In [R] vs. time plot is given alongside.

[HOTS]

For this reaction

- i. what is the order of the reaction?
- ii. what are the units of rate constant k?
- iii. give the relationship between k and $t_{1/2}$ (half-life period).
- iv. what is the slope of the curve?
- v. **dr**aw the plot $\log [R]_0 / [R]$ vs time t(s).



Ans.

i. First order ii. time⁻¹ (s⁻¹) iii. $k = \frac{0.693}{t_{1/2}}$ iv. slope = -k (rate constant)



(v)

Q.4. Answer the following questions:

Q. Graphically explain the effect of temperature on the rate constant of reaction. How can this temperature effect on rate constant be represented quantitatively?

Ans. Increasing the temperature of a reaction mixture increased the fraction of molecules which colloide with energies greater than E_a . It is clear from the graph below that with 10°C rise in temperature the area showing the fraction of molecules having energy equal to or greater than activation energy gets almost double leading to almost to doubling the rate constant. Quantitatively the effect of temperature on rate constant (*k*) is given by Arrhenius equation.

$$k = A e^{-E_a/RT}$$
 or $k = A \frac{1}{e^{E_a/RT}}$

where A is the frequency factor, R is the gas constant and E_a is the activation energy.



Thus, from Arrhenius equation we find that increasing the temperature or decreasing the activation energy will result in an exponential increase in rate constant.

Q.The decomposition of a hydrocarbon follows the equation

 $k = (4.5 \times 10^{11} s^{\text{--}1}) e^{-28000 \ K/T}$

Calculate Ea.

Ans.

Comparing with Arrhenius equation $k={
m Ae}^{-E_a/\,{
m RT}}$, we get

$$-\frac{E_a}{RT} = -\frac{28000 K}{T}$$
 or $E_a = 28000 K \times R$

 $E_a = 28000 \text{ K} \times 8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} = 232792 \text{ J} \text{ mol}^{-1}$

 $E_a = 232.79 \text{ kJ mol}^{-1}$

Q.5. Answer the following questions:

Q. Write the rate law for a first order reaction. Justify the statement that half life for a first order reaction is independent of the initial concentration of the reactant.

Ans. Consider the first order reaction,

$$R \rightarrow P$$

For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

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

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{|R|_0}{|R|}$$
, where $[R]_0$ = initial concentration, $[R]$ = concentration at time t .

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

So, the above equation becomes

$$egin{aligned} t_{1/2} &= rac{2.303}{k} \log rac{/R_{l_0}}{/R_{l_0}/2} \ t_{1/2} &= rac{2.303}{k} \log 2 \quad ext{or} \quad t_{1/2} &= rac{2.303}{k} imes \ 0.3010 \ t_{1/2} &= rac{0.693}{k} \end{aligned}$$

Q. The activation energy of a reaction is 75.2 kJ mol⁻¹ in the absence of a catalyst and it lowers to 50.14 kJ mol⁻¹ with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25° C?

Ans. According to Arrhenius equation,

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

For uncatalysed reaction,

For catalysed reaction,

$$\log k_1 = \log A - \frac{E_{a_1}}{2.303 \text{ RT}} \dots (i)$$

$$\log k_2 = \log A - \frac{E_{a_2}}{2.303 \text{ RT}}...(ii)$$

A is equal for both reactions.

Subtracting equation (i) from equation (ii),

$$\log rac{k_2}{k_1} = rac{E_{a_1} - E_{a_2}}{2.303 \ ext{RT}} = rac{(75.2 - 50.14) \ ext{kJ mol}^{-1}}{2.303 imes 8.314 \ ext{JK}^{-1} \ ext{mol}^{-1} imes 298 \ ext{K}} = 4.39$$

 $rac{k_2}{k_1} = ext{anti} \log \ (4.39) = \ 2.45 imes 10^4$

Rate of reaction increases by 2.45×10^4 times.

Q.6. Answer the following questions:

Q. In the reaction

$Q + R \rightarrow P \textbf{r}o \textbf{d}ucts$

The time taken for 99% reaction of Q is twice the time taken for 90% reaction of **R**. The concentration of **R** varies with time as shown in the figure given alongside.



What is the overall order of the reaction? Give the units of the rate constant for the same. Write the rate expression for the above reaction.

Ans. For reactant Q, $t_{99\%} = 2 \times t_{90\%}$

Therefore, order of reaction w.r.t. reactant Q = 1.

From the graph, order of reaction w.r.t. reactant, R = 0.

So, overall order of reaction = 1 + 0 = 1

Unit of rate constant, $k = time^{-1}$

Rate = $k[Q][R]^0$

Rate = k[Q]

Q. Rate constant for a first order reaction has been found to be 2.54×10^{-3} s⁻¹.

Calculate its three-fourth life.

Ans.

$$[R] = [R]_0 - \frac{3}{4}[R]_0 = \frac{/R_0}{4}$$

Substituting $[R] = \frac{/R_{l_0}}{4}$, $k = 2.54 \times 10^{-3} \ s^{-1}$ in the expression $t = \frac{2.303}{k} \log \frac{/R_{l_0}}{/R}$, we get

$$t = rac{2.303}{2.54 imes 10^{-3}} \log rac{/R_{
m o}}{/R_{
m o}/4} = rac{2.303 imes 10^3}{2.54} \log 4$$
 $t = rac{2.303 imes 10^3}{2.54} imes \ 0.6021 = 545.92 \ s$

Alternative Method:

For a first order reaction, $t_{3/4} = 2 \times t_{1/2}$

 $egin{array}{lll} \dot{\ } t_{3/4} = 2 imes rac{0.693}{k} \ t_{3/4} = rac{2 imes 0.693}{2.54 imes 10^{-3} s} = 545.67 \; s \end{array}$