CH-4 Chemical Kinetics

Ques 1.   Define 'order of a reaction'.

Ans 1.   The sum of powers of the concentration of the reactants in the rate law expression is called the order of reaction.

Ques 2.   Write two differences between 'order of reaction' and 'molecularity of reaction'.

Ans 2.   The differences are as follows:

Order of reaction	Molecularity of reaction
It is the sum of tire concentration terms on which die rate of reaction actually depends.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It can be fractional as well as zero.	It is always a whole number.

Ques 3.   Express the rate of the following reaction in terms of the formation of ammonia :
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Ans 3.   Rate of reaction

$$\frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

Ques 4.   Define the following terms :
(a) Pseudo first order reaction.
(b) Half-life period of reaction ($t_{1/2}$).

Ans 4.   (a) Those reactions which are not truly of the first order but under certain conditions become first order reactions are called pseudo first order reaction.
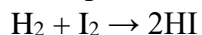(b) The time taken for half of the reaction to complete is called half-life period.

Ques 5.   Define the following:
(i) Elementary step in a reaction
(ii) Rate of a reaction

Ans 5.   **(i) Elementary step in a reaction:** Those reactions which take place in one step are called elementary reactions.

Example : Reaction between H_2, and I_2 to form 2HI

$H_2 + I_2 \rightarrow 2HI$

(ii) Rate of a reaction: The change in the concentration of any one of the reactants or products per unit time is called rate of reaction.

Ques 6. **If the rate constant of a reaction is k = 3×10^{-4} s^{-1}, then identify the order of the reaction.**

Ans 6.   sec^{-1} is the unit for rate constant of first order reaction.

Ques 7. **Write the unit of rate constant for a zero-order reaction.**

Ans 7.   Mol L^{-1} sec^{-1} is unit of rate constant for a zero-order reaction.

Ques 8. **Define rate constant (K).**

Ans 8.   It is defined as the rate of reaction when the concentration of each reactant is taken as unity.

Ques 9. **For a reaction R $\rightarrow$ P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?**

Ans 9.   The $t_{1/2}$ of a first order reaction is independent of initial concentration of reactants.

Ques 10. **A reaction is of second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is (i) doubled, (ii) reduced to half?**

Ans 10.   Since Rate = $K[A]^2$
For second order reaction Let $[A] = a$ then Rate = Ka^2
(i) If $[A] = 2a$ then Rate = $K(2a)^2 = 4Ka^2$
∴Rate of reaction becomes 4 times

(ii) If $[A] = a2$ then Rate = $K(a2)2 = Ka24$
∴ Rate of reaction will be 14 th .

Ques 11. **A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when (i) the concentration of B alone is increased to three times (ii) the concentrations of A as well as B are doubled?**

Ans 11.   Rate = $K[A]^1 [B]^2$
(i) When concentration of B increases to 3 times, the rate of reaction becomes 9 times
$r = KA(3B)^2$ ∴ $r = 9KAB^2 = 9$ times
(ii) $r = K(2A)(2B)^2$ ∴ $r = 8KAB^2 = 8$ times

Ques 12. **Write the rate equation for the reaction $A_2 + 3B_2 \rightarrow 2C$, if the overall order of the reaction is zero.**

Ans 12. $A_2 + 3B_2 \rightarrow 2C$
Rate = $(dx/dt) = K[A]^0 [B]^0 = K$ (rate constant)

Ques 13. **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 13.   For a zero order reaction,

$$\text{Time, } t = \frac{1}{K}[(A)_0 - (A)]$$

$$\text{or, } t = \frac{1}{0.003}(0.10 - 0.075)$$

$$\therefore \quad \text{Time, } t = \frac{1}{0.003} \times \frac{0.025}{1} = \frac{25}{3} = 8.3 \text{ seconds}$$

Ques 14. **What do you understand by the rate law and rate constant of a reaction? 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}

Ans 14.   The rate of reaction is found to depend on α concentration of term of reactant A and β
concentration term of reactant B
Then Rate of reaction $\propto [A]_\alpha [B]_\beta$
or Rate = $K [A]_\alpha [B]_\beta$
This expression is called Rate law.
'K' in this expression is called Rate constant. Rate constant's unit :
(i) Unit = L^{-1} mol s^{-1} → Zero order reaction
(ii) Unit = L mol^{-1} s^{-1} → Second order reaction.

Ques 15. **The thermal decomposition of HCO_2H is a first order reaction with a rate constant of 2.4×10^{-3} s^{-1} at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO_2 H to decompose. (log 0.25 = -0.6021)**

Ans 15.   Given: $K = 2.4 \times 10^{-3}$

$$\text{According to the formula, where} \begin{cases} a = 1 \\ K = 2.4 \times 10^{-3} \\ x = \frac{3}{4} = 0.75 \end{cases}$$

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

Putting these values in the above equation

$$t = \frac{2.303}{K} \log \frac{1}{1-0.75}$$

$$\text{or} \quad t = \frac{2.303}{2.4 \times 10^{-3}} \log 0.25$$

$$\text{or} \quad t = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6020$$

$$\text{or} \quad t = \frac{1.386406}{2.4 \times 10^{-3}} = 577.6$$

$$\therefore \quad \textbf{Time taken, } t = \textbf{577.6 sec.}$$

Ques 16. **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?**

Ans 16. Rate = K $[A]^2$ = Ka^2
If [A] = 12a Rate = K (a2)2=14 Ka^2
∴ Rate = $1/4^{th}$ (one fourth of origina rate)
The unit of rate constant is L mol^{-1} s^{-1}

Ques 17. **A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (ii) reduced to half?**

Ans 17. As Formula, r = K$[R]^2$ …(Given)
(i) R' = 2R $\Rightarrow$ r = K$[2R]^{-1}$ = 4KR^{-1}
∴ Rate becomes 4 times than original rate

(ii) R' = $\frac{1}{2}$R $\qquad \Rightarrow r = K\left[\dfrac{R}{2}\right]^2 = \dfrac{K}{4}R^2$

∴ Rate becomes $\dfrac{1}{4}$ of the original rate

Ques 18. **(a) For a reaction A + B → P, the rate law is given by, r = k$[A]^{1/2}$ $[B]^2$. What is the order of this reaction?**
(b) A first order reaction is found to have a rate constant k = 5.5 × 10^{-14} s^{-1}. Find the half-life of the reaction.

Ans 18. (a) According to the formula : r = k$[A]^{1/2}$ $[B]^2$

Order w.r.t. A = $\dfrac{1}{2}$, Order w.r.t B = 2

∴ Overall order = $\dfrac{1}{2} + \dfrac{2}{1} = \dfrac{5}{2}$

(b) For first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

Given: k = 5.5 × 10^{-14} s^{-1}

Thus, $t_{1/2} = \dfrac{0.693}{5.5 \times 10^{-14} s^{-1}}$

Hence $t_{1/2}$ = **1.26 × 10^{13}s**

Ques 19. **Rate constant k for a first order reaction has been found to be 2.54 × 10^{-3} sec^{-1}. Calculate its 3/4th life, (log 4 = 0.6020).**

Ans 19. For first order reaction:

$t_{3/4} = \dfrac{2.303}{k}$ log 4

$= \dfrac{2.303}{2.54 \times 10^{-3} sec^{-1}} \times 0.6020 = 545.8$ sec.

= **9.09 min.**

Ques 20. A first order gas phase reaction : $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}$ sec^{-1}. What percentage of A_2B_2 is decomposed on heating for 900 seconds? (Antilog 0.0781 = 1.197)

Ans 20. Since the reaction is of the first order

$$\therefore \quad k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \log \frac{100}{x} = 0.781$$

Given : $k = 2.0 \times 10^{-4}$ sec^{-1}, $t = 900$ sec

Substituting these values, we get

$$2.0 \times 10^{-4} = \frac{2.303}{900} \log \frac{a}{a-x}$$

$$\Rightarrow \quad \log \frac{a}{a-x} = \frac{2.0 \times 10^{-4} \times 900}{2.303}$$

$$\Rightarrow \quad \log \frac{a}{a-x} = 0.0781$$

$$\Rightarrow \quad \frac{a}{a-x} = \text{antilog} (0.0781) = 1.197$$

$$\Rightarrow \quad a = 1.197\, a - 1.197\, x$$

$$\Rightarrow \quad 0.197\, a = 1.197\, x$$
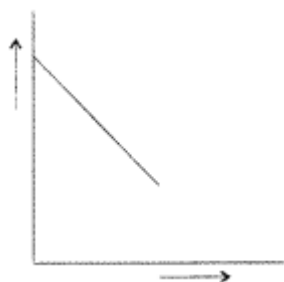
$$\therefore \quad \frac{x}{a} = \frac{0.197}{1.197} = 0.1645$$

$$\therefore \quad \% \text{ decomposed} = 0.1645 \times 100 = \mathbf{16.45\%}$$

Ques 21. For a chemical reaction $R \rightarrow P$, the variation in the f concentration (R) vs. time (f) plot is given as
(i) Predict the order of the reaction.
(ii) What is the slope of the curve? (All India 2014)

Ans 21. (i) It is zero order reaction.
(ii) Slope of the curve = -K

Ques 22. (a) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction?
(b) Write the unit of rate constant 'k' for the first order reaction.

Ans 22. (a) For a reaction, $A + B$
Rate = $k [A]^1 [B]^2$
This is the third order of reaction.
(b) Unit of rate constant for first order reaction is S^{-1}

Ques 23. **A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half?**

Ans 23. Since Rate = $K[A]^2$
For second order reaction Let $[A] = a$ then Rate $= Ka^2$
(i) If $[A] = 2a$ then Rate $= K(2a)^2 = 4\,Ka^2$
∴Rate of reaction becomes 4 times
(ii) If $[A] = a2$ then Rate $= K(a2)2 = Ka24$
∴ Rate of reaction will be 14 th .

Ques 24. **For a chemical reaction R → P, variation in ln[R] vs time (f) plot is given below:**
For this reaction:
(i) Predict the order of reaction
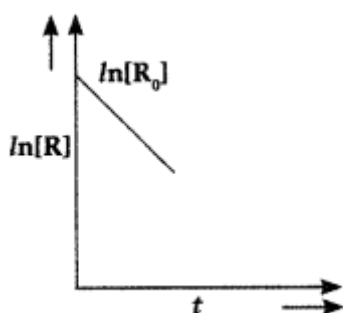
(ii) What is the unit of rate constant (k)? (Comptt. Delhi 2017)

Ans 24. (i) It is zero order reaction.
(ii) The unit of rate constant (k) is mol L^{-1} S^{-1}.

Ques 25. **(i) What is the order of the reaction whose rate constant has same units as the rate of reaction?**
(ii) For a reaction A + H₂O → B; Rate ∝ [A],
What is the order of this reaction?

Ans 25. (i) The reaction whose rate constant has same units as the rate of reaction, will have zero order of reaction.
(ii) The reaction A + H₂O → B Rate ∝ [A]
First order reaction as the rate of reaction depends only on concentration of A only.

Ques 26. **Write units of rate constants for zero order and for the second order reactions if the concentration is expressed in mol L^{-1} and time in second.**

Ans 26. Using formula of rate constant,
$K = [\text{mol } L^{-1}]^{1-n}\, s^{-1}$ (n = order of rxⁿ)
Unit for zero order reaction,
$K = [\text{mol } L^{-1}]^{1-0}\, s^{-1}$
$K = [\text{mol } L^{-1}]\, s^{-1} = \text{mol } L^{-1}\, s^{-1}$
Unit for second order reaction,
$K = [\text{mol } L^{-1}]^{1-2} = [\text{mol } L^{-1}]^{-1}\, s^{-1}$

Ques 27. For a reaction: $H_2 + Cl_2 \longrightarrow 2HCl$
Rate = k
(i) Write the order and molecularity of this reaction.
(ii) Write the unit of k.

Ans 27. $H_2 + Cl_2 \longrightarrow 2HCl$
This reaction is zero order reaction and molecularity is two.
(ii) Unit of $k = mol\ L^{-1}\ s^{-1}$

Ques 28. A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, what concentration of reactant will remain in solution after 3 hours?

Ans 28. Given : $[R]_0 = 0.10$ M, $t = 3$ hrs = 180 min
$K = 0.0051$ min^{-1} $[R] = ?$

$$Using\ formula : K = \frac{2.303}{t} \log \frac{[R]_o}{[R]}$$

$$\therefore \quad 0.0051 = \frac{2.303}{180} \log \frac{0.10}{[R]}$$

$$or \quad \log \frac{0.10}{[R]} = \frac{0.0051 \times 180}{2.303}$$

$$or \quad \log \frac{0.10}{[R]} = \frac{0.918}{2.303} = 0.3986$$

$$or \quad \frac{0.10}{[R]} = antilog\ (0.3986)$$

$$or \quad \frac{0.10}{[R]} = 2.503$$

$$\therefore \quad [R] = \frac{0.10}{2.503} = 0.0399$$

$\therefore$ Concentration of reactant remains 0.040 M

Ques 29. Nitrogen pentoxide decomposes according to equation :
$2N_2O_5(g) \longrightarrow 4\ NO_2(g) + O_2(g)$.
This first order reaction was allowed to proceed at 40°C and the data below were collected :

[N$_2$O] (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0

Calculate the rate constant. Include units with your answer.
(b) What will be the concentration of N$_2$O$_5$ after 100 minutes?
(c) Calculate the initial rate of reaction.

Ans 29. (a) $K = 2.303t\log[A_0]/[A]$
Substituting the values, we get

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

or $\quad K = \frac{2.303}{20} \log 1.3840$

or $\quad K = 0.11515 \log 1.3840$

$\therefore \quad \mathbf{K = 0.0163\ min^{-1}}$

(b) $K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$

$\therefore \quad 0.0163 = \frac{2.303}{100} \log \frac{0.400}{[A]}$

or $\quad \log \frac{0.400}{[A]} = \frac{0.0163 \times 100}{2.303}$

or $\quad \log \frac{0.400}{[A]} = 7.0777$

$\therefore \quad \mathbf{[A] = 0.078\ M}$

(c) Initial Rate, $R = K\ [N_2O_5]$
$$= 0.0163\ min^{-1}\ (0.400\ M)$$
$$= \mathbf{0.00652\ M\ min^{-1}}$$

Ques 30. For the reaction
$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ the following data were collected. All the measurements were taken at 263 K :

Experiment No.	Initial [NO](M)	Initial [Cl$_2$](M)	Initial rate of disappearance of Cl$_2$ (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.
(b) Calculate the value of rate constant and specify its units.
(c) What is the initial rate of disappearance of Cl$_2$ in exp. 4?

Ans 30. (a) Rate law $= K[NO]^2\ [Cl_2]$
(b) $0.60\ M\ min^{-1} = K[0.15]^2\ [0.15]\ M^3$
$\therefore K = 177.7\ M^{-2}\ min^{-1}$
(c) Initial rate of disappearance of Cl_2 in exp. 4
Formula : Rate $= K[NO]^2\ [Cl_2]$

$\therefore$ Initial rate $= 177.7 M^{-2} min^{-1} \times (0.25)^2 \times (0.25) M^3$
$= 2.8\ M\ min^{-1}$

Ques 31. Following data are obtained for the reaction:
$N_2O_5 \rightarrow 2NO_2 + 12O_2$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.
(b) Calculate the half-life.
(Given log 2 = 0.3010 log 4 = 0.6021)

Ans 31.   (a) For first order reaction:

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

$$k = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

At $t = 300$ s

$$k = \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}}$$

$$= \frac{2.303}{300} \log 2 = \frac{2.303}{300} \times 0.3010$$

$\therefore$ $k = 0.0023106$

At $t = 600$ s

$$k = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}}$$

$$= \frac{2.303}{600} \log 4 = \frac{2.303}{600} \times 0.6020$$

$\therefore$ $k = 0.0023106$

Since the value of k comes to nearly constant
therefore it follows the first order reaction.

(b) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.0023106} = 299.9 = \mathbf{300\ s}$

Ques 32. A reaction is first order in A and second order in B.
(i) Write differential rate equation.
(ii) How is rate affected when concentration of B is tripled?
(iii) How is rate affected when concentration of both A and B is doubled?

Ans 32.   (i) Differential rate equation :
dx/dt = rate = K $[A]^1 [B]^2$
(ii) Rate, $r_1 =$ K $[A]^1[B]^2$ …………… (i)
When concentration of B is increased three times then
Rate, $r_2 =$ K $[A]^1 [3B]^2$ ………..(ii)

Dividing equation (ii) by (i) we get

$r_2 = 9r_1$ rate increases by nine times.

(iii) When concentration of both A and B are doubled, then

$r_3 = K [2A]^1 [2B]^2$ ………….. (iii)

Dividing equation {Hi) by (t), we get

$r_3 = 8r_1$

Hence rate increases by eight times.

Ques 33. **The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:**

$$SO_2Cl_2 (g) \rightarrow SO_2 (g) + Cl_2(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

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

Ans 33. $SO_2Cl_2 (g) \rightarrow SO_2 (g) + Cl_2(g)$

Using formula, $K = 2.303/t \; (\log P_0/2P_0 - P_t)$

When t = 100 s

$$K = \frac{2.303}{100 \, s} \log \frac{0.4}{2 \times 0.4 - 0.7}$$

$$= \frac{2.303}{100 \, s} \log \frac{0.4}{0.8 - 0.7} = \frac{2.303}{100 \, s} \log \frac{0.4}{0.1}$$

$$= \frac{2.303}{100 \, s} \log \frac{4}{1} = \frac{2.303}{100} \log 4$$

$$= \frac{2.303}{100} \times 0.6021 = \mathbf{1.386 \times 10^{-2} \; s^{-1}}$$

Ques 34. **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 its l/10th value?**

Ans 34. Given: $k = 60 \; s^{-1}$, t =?

If initial concentration is $[A_0]$

Then $\frac{1}{10}$ th of initial concentration is $\frac{[A_0]}{10}$

Using expression for first order reaction,

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \qquad t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

Substituting values,

$$t = \frac{2.303}{60 \, s^{-1}} \log \frac{[A_0]}{[A_0]/10} \Rightarrow t = \frac{2.303}{60 \, s^{-1}} \log 10$$

$$\Rightarrow t = \frac{2.303}{60 \, s^{-1}} \times 1 \qquad \therefore t = 0.0383 \; s$$

Ques 35. If the half-life period of a first order reaction in A is 2 minutes, how long will it take [A] to reach 25% of its initial concentration?

Ans 35.

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

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

$$2 \text{ min} = \frac{2.303}{k} \log 2 \qquad \qquad ...(i)$$

$$t_{75\%} = \frac{2.303}{k} \log \frac{100}{25}$$

$$t_{75} = \frac{2.303}{k} \log 4 \qquad \qquad ...(ii)$$

Divide (i) by (ii)

$$\frac{t_{75\%}}{2\min} = \frac{\log 4}{\log 2} = \frac{2\log 2}{\log 2}$$
$$t_{75} = 4 \text{ min}$$

Ques 36. Hydrogen peroxide, H_2O_2 (aq) decomposes to H_2O (l) and O_2 (g) in a reaction that is first order in H_2O_2 and has a rate constant k = 1.06×10^{-3}min^{-1}.
(i) How long will it take for 15% of a sample of H_2O_2 to decompose?
(ii) How long will it take for 85% of the sample to decompose?

Ans 36.   (i) Given: k = 1.06×10^{-3}min^{-1}
For first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{where } [x = \frac{15}{100}a = 0.15a$$

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

$$\text{or} \quad t = \frac{2.303}{1.06 \times 10^{-3}} \log \frac{a}{a-0.15a}$$

$$t = 2172.64 \log 1.1764$$

$$\therefore \quad \text{Time } (t) = 2172.64 \times 0.07055$$
$$= \textbf{153.29 min}$$

$$(ii) \ t = \frac{2.303}{k} \log \frac{a}{a-x} \qquad \text{[For 85\% completion}$$

$$t = \frac{2.303}{1.06 \times 10^{-3}} \log \frac{a}{a-0.85a}$$

$$= 2172.64 \log 6.66$$

$$\therefore \quad \text{Time } (t) = 2172.64 \times 0.8234$$
$$= \textbf{1789.11 min}$$

Ques 37. For the first order thermal decomposition reaction, the following data were obtained:

$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant (Given: log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

Ans 37.

Given: Initial pressure, $P_0 = 0.30$ atm

$$P_t = 0.50 \text{ atm}$$
$$t = 300 \text{ s}$$

Rate constant, $k = \dfrac{2.303}{t} \log \dfrac{P_0}{2P_0 - P_t}$

$$= \dfrac{2.303}{300 \text{ s}} \log \dfrac{0.30}{2 \times 0.30 - 0.50}$$

$$= \dfrac{2.303}{300 \text{ s}} \log \dfrac{0.30}{0.60 - 0.50}$$

$$= \dfrac{2.303}{300 \text{ s}} \log \dfrac{0.30}{0.10} = \dfrac{2.303}{300 \text{ s}} \log 3$$

$$= \dfrac{2.303}{300 \text{ s}} \times 0.4771 = \dfrac{1.099}{300 \text{ s}}$$

$$= 0.0036 \text{ s}^{-1} \quad \text{or} \quad 3.66 \times 10^{-3} \text{s}^{-1}$$

Ques 38. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Ans 38.

$$\therefore \quad t_{99\%} = \dfrac{2.303}{K} \log \dfrac{a}{a - 0.99a}$$

$$= \dfrac{2.303}{K} \log 10^2 = 2 \times \dfrac{2.303}{K}$$

90% completion means that x
$$= 90\% \text{ of } a = 0.90a$$

$$\therefore \quad t_{90\%} = \dfrac{2.303}{K} \log \dfrac{a}{a - 0.90a}$$

$$= \dfrac{2.303}{K} \log 10 = \dfrac{2.303}{K}$$

$$\therefore \quad \dfrac{t_{99^\circ}}{t_{90^\circ}} = \dfrac{\left(\dfrac{2 \times 2.303}{K}\right)}{\left(\dfrac{2.303}{K}\right)} = 2$$

$$\therefore \quad t_{99\%} = 2 \times t_{90\%}$$

Ques 39. If half-life period of a first order reaction is x and 3/4,[th] life period of the same reaction is y, how are x and y related to each other?

Ans 39. $t_{1/2} = 0.693K$ (For first order reaction)
$t_{3/4} = K \Rightarrow t_{3/4} = 1.3864K$
According to condition
From the above equation it is clear that
$t_{3/4} = 2t_{1/2} \therefore y = 2X$ (The value 1.3864 is double of 0.693)

Ques 40. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.
(Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)

Ans 40.   Given:
$t = 20$ min, $A_0 = 100\%$, $A = 100 - 25 = 75\%$, $k = ?$

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

$$= \frac{2.303}{20} \log \frac{100}{75}$$

$$= \frac{2.303}{20} \log 1.33$$

$$= \frac{2.303}{20} \times 0.1248$$

$\therefore k = 0.0143 \ \text{min}^{-1}$
So for 75% completion of reaction,

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

$$= \frac{2.303}{0.0143} \log \frac{100}{25}$$

$$= \frac{2.303}{0.0143} \log 4$$

$$\therefore t = \frac{2.303}{0.0143} \times 0.6021 = \textbf{96.96 min}$$

Ques 41. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

Experiment	Time(s)	Total pressure (atm)
1	0	0.4
2	100	0.7

Calculate the rate constant (k).
[Given : log 2 = 0.3010; log 4 = 0.6021] (Comptt. Delhi 2016)

Ans 41. $SO_2Cl_2 (g) \rightarrow SO_2 (g) + Cl_2(g)$

Using formula, $K = \dfrac{2.303}{t} \log \dfrac{P_0}{2P_0 - P_t}$

When t = 100 s

$$K = \dfrac{2.303}{100\,s} \log \dfrac{0.4}{2 \times 0.4 - 0.7}$$

$$= \dfrac{2.303}{100\,s} \log \dfrac{0.4}{0.8 - 0.7} = \dfrac{2.303}{100\,s} \log \dfrac{0.4}{0.1}$$

$$= \dfrac{2.303}{100\,s} \log \dfrac{4}{1} = \dfrac{2.303}{100} \log 4$$

$$= \dfrac{2.303}{100} \times 0.6021 = \mathbf{1.386 \times 10^{-2} \ s^{-1}}$$

Ques 42. A first order reaction is 15% completed in 20 minutes. How long will it take to complete 60% of the reaction?

Ans 42. For the first order reaction

$$K = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$$

I^{st} **case** : $a = 100$, $x = 15$, time, $t = 20$ minutes

$(a - x) = 100 - 15 = 85$

$$t^{15\%} = \dfrac{2.303}{K} \log \dfrac{100}{85}$$

$$\therefore \quad 20 = \dfrac{2.303}{K} \log \dfrac{100}{85} \qquad\qquad ...(i)$$

IInd **case** : $a = 100$, $\quad x = 60$, $\qquad$ time, $t_{60\%} = ?$

$(a - x) = 100 - 60 = 40$

$$t_{60\%} = \dfrac{2.303}{K} \log \dfrac{100}{40} \qquad\qquad ...(ii)$$

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

$$\dfrac{t_{60\%}}{20} = \dfrac{\log \dfrac{100}{40}}{\log \dfrac{100}{85}} = \dfrac{\log 100 - \log 40}{\log 100 - \log 85}$$

$$= \dfrac{2.000 - 1.6021}{2.0000 - 1.9294}$$

$$\dfrac{t_{60\%}}{20} = \dfrac{0.3979}{0.0706} = 5.64$$

$\therefore \quad t_{60\%} = 20 \times 5.64 = \mathbf{112.8 \ minutes}$
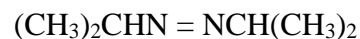
Ques 43. For the first order decomposition of azoisopropane to hexane and nitrogen at 543 K , the following data were obtained :
Calculate the rate constant. The equation for the reaction is:

Experiment	Time(s)	Total (mmHg)
1	0	35.0
2	720	63.0

$(CH_3)_2CHN = NCH(CH_3)_2 \rightarrow C_6H_{14}$ (g) + N_2 (g)
[Given : log 3 = 0.4771; log 5 = 0.6990]

Ans 43. $(CH_3)_2CHN = NCH(CH_3)_2$ N_2 C_6H_{14}

Initial pressure	P_0	O	O
After time t	$P_0 - P$	P	P

Total Pressure after time t$(P_t) = (P_0 - P) + P + P$

$P = P_t - P_0$

$a \propto P_0$

$(a - x) \propto P_0 - P$

Substituting the value of P

$a - x \propto P_0 - (P_t - P_0)$

or, $(a - x) \propto P_0 - P_t$

As decomposition of azoisopropane is a first order reaction

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

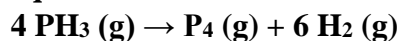$$K = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When $t = 720$ s

$$K = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0}$$

$$= \frac{2.303}{720 \text{ s}} \log 5 = \frac{2.303}{720} \times (0.6990)$$

$$\therefore \quad K = 2.235 \times 10^{-3} \text{ s}^{-1}$$

Ques 44. The decomposition of phosphine, PH_3, proceeds according to the following equation:

$4 PH_3$ (g) $\rightarrow P_4$ (g) + 6 H_2 (g)

It is found that the reaction follows the following rate equation :

Rate = K [PH_3].

The half-life of PH_3 is 37.9 s at 120° C.

(i) How much time is required for 3/4th of PH_3 to decompose?

(it) What fraction of the original sample of PH_3 remains behind after 1 minute?

Ans 44. **(i)** According to the formula :

$$K = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \qquad \qquad ...(i)$$

$$\text{and} \quad K = \frac{0.693}{t_{1/2}} \qquad \qquad ...(ii)$$

On comparing both equations

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\text{or} \quad t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{[A]_0}{[A]}$$

Let initial conc^n = a i.e. $[A]_0$

$$\text{then} \quad t = \frac{2.303 \times 37.9}{0.693} \log \frac{a}{a - \frac{3}{4}a}$$

$$\text{or} \quad t = \frac{2.303 \times 37.9}{0.693} \log 4$$

$$\text{or} \quad t = \frac{87.2837}{0.693} \times 0.6020 = 75.8$$

∴ **Time required to decompose, t = 75.8 seconds**

(ii) $K = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)}$

$$\frac{0.693}{(37.9s)} = \frac{2.303}{60s} \log \frac{a}{(a-x)}$$

$$\log \frac{a}{(a-x)} = \frac{0.693}{37.9} \times \frac{60}{2.303}$$

$$= 0.4764 = 2.995$$

$$\frac{a}{a-x} = \text{Antilog } 0.4764$$

If $a = 1$, then $(a - x)$ i.e. fraction left may be calculated as :

$$\frac{1}{(a-x)} = 2.995$$

∴ **Fraction of original sample,**

$$(a - x) = \frac{1}{2.995} = 0.334$$

Ques 45. **(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 on 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)

Ans 45.   (a) (i) Differential rate equation :
dxdt = K [A]^2[B]
(ii) When concentration of A is increased to three times, the rate of reaction becomes 9 times
r = K[3A]^{2}B ∴ r = 9KA^{2}B i.e. = 9 times
(iii) r = K[2A]^2[2B] ∴ r = 8KA^{2}B i.e. = 8 times

(b) Given : Time, t = 40 minutes, t =?
Let a = 100, ∴ x = 30% of 100 = 30
Using the formula :

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

$$\text{or } 40 = \frac{2.303}{K} \log \frac{100}{100-30}$$

$$\text{or } K = \frac{2.303}{40} \log \frac{100}{70}$$

$$\text{or } K = \frac{2.303}{40} (\log 10 - \log 7)$$

$$\text{or } K = \frac{2.303}{40} (1 - 0.8451)$$

$$\text{or } K = \frac{2.303}{40} \times 0.1549$$

$$\text{or } K = \frac{0.3567}{40} = 0.0089 \text{ min}$$

$$\therefore t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.0089} = \textbf{77.86 min.}$$

Ques 46. A first order reaction takes 100 minutes for completion of 60% of the reaction.
Find the time when 90% of the reaction will be completed.

Ans 46. For the first order reaction,

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

When reaction is 60% complete

$$x = \frac{60}{100} a = 0.6a,$$

$$t = 100 \ min^{-1} \qquad\qquad (Given)$$

then $k = \dfrac{2.303}{100} \log \dfrac{a}{a-0.6a}$

$\Rightarrow \quad k = \dfrac{2.303}{100} \log \dfrac{a}{0.4a}$

$\Rightarrow \quad k = \dfrac{2.303}{100} \log 2.5 \qquad\qquad ...(i)$

$t = ?, \ \textit{when reaction is 90\% complete}$

$x = 0.9a$

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

$\Rightarrow \quad k = \dfrac{2.303}{t} \log \dfrac{a}{a-0.9a}$

$\Rightarrow \quad k = \dfrac{2.303}{t} \log 10 \qquad\qquad ...(ii)$

Taking equations (*i*) and (*ii*), we get

$$\frac{2.303}{100} \log 2.5 = \frac{2.303}{t} \log 10$$

$\Rightarrow \quad \dfrac{0.3979}{100} = \dfrac{1}{t} \qquad \Rightarrow t = \dfrac{100}{0.3979}$

$\therefore \quad t = 251.31 \ \textbf{minutes}$

Ques 47. **For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:**

t/s	0	30	60
[CH₃COOCH₃]/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)

Ans 47.

$$(i)\ k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k_1 = \frac{2.303}{30}\log\frac{0.60}{0.30} \qquad\qquad k_2 = \frac{2.303}{60}\log\frac{0.60}{0.15}$$

$$k_1 = \frac{2.303}{30}\times\log 2 \qquad\qquad k_2 = \frac{2.303}{60}\times\log 4$$

$$k_1 = \frac{2.303}{30}\times 0.3010\ \text{sec}^{-1} \qquad k_2 = \frac{2.303}{60}\times 2\log 2$$

$$k_1 = 2.31\times 10^{-2}\ \text{sec}^{-1} \qquad\qquad k_2 = \frac{2.303\times 2\times 0.3010}{60}$$

$$k_2 = 2.31\times 10^{-2}\ \text{sec}^{-1}$$

As k is constant in both the readings, hence it is a pseudo first order reaction.

(ii) Rate $= -\Delta[R]/\Delta t$, Average rate between 30 to 60 seconds
$= -(0.15-0.30)60-30 = 0.1530$
$= 0.5\times 10^{-2}\ \text{mol L}^{-1}\ \text{sec}^{-1}$

Ques 48. (a) For a reaction A + B → P, the rate is given by Rate = k[A] [B]^2
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess?
(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.
(log 2 = 0.3010)

Ans 48. (a) For the reaction A + B → P rate is given
by Rate $= k[A]^1[B]^2$
(i) $r_1 = k[A]1\ [B]2$
$r_2 = k[A]^1[2B]^2 =$
$r_2 = k[A]^1\ [2B]^2 = 4k[A]^1\ [B]^2$
$r_1 = 4r_2$, rate will increase four times of actual rate.

(ii) When A is present in large amount, order w.r.t. A is zero.
Hence overall order $= 0 + 2 = 2$, second order reaction.

$$(b)\ t_{\frac{1}{2}} = 30\ \text{minutes},\quad t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$\Rightarrow\quad 30\ \text{min} = \frac{0.693}{k}$$

$$\Rightarrow\quad k = \frac{0.693}{30}\ \text{min}^{-1} \quad\Rightarrow k = 0.0231\ \text{min}^{-1}$$

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

$$t = \frac{2.303}{0.0231}\log\frac{100}{10} \quad\Rightarrow t = \frac{2.303}{0.0231}\ \text{min}$$

$$\therefore\quad t = \textbf{99.7 minutes}$$

Ques 49. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	10	20
$[CH_3COOCH_3]$/mol L^{-1}	0.10	0.05	0.025

(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 10 to 20 seconds. (Given : log 2 = 0.3010, log 4 = 0.6021)

Ans 49.

(i) $[A]_0 = 0.10$ mol/L, $[A] = 0.5$ mol/L, $t = 10$s
$[A]_0 = 0.10$ mol/L, $[A] = 0.25$ mol/L, $t = 20$s

$k = \dfrac{2.303}{t}\log\dfrac{[A_0]}{[A]}$ 　　　　$k = \dfrac{2.303}{t}\log\dfrac{[A_0]}{[A]}$

$k_1 = \dfrac{2.303}{10}\log\dfrac{0.1}{0.05}$ 　　　　$k_2 = \dfrac{2.303}{20}\log\dfrac{0.1}{0.025}$

$k_1 = \dfrac{2.303}{10}\times\log 2$ 　　　　$k_2 = \dfrac{2.303}{20}\times\log 4$

$k_1 = \dfrac{2.303\times 0.3010}{10}$ 　　　　$k_2 = \dfrac{2.303\times 2\log 2}{20}$

$k_1 = \dfrac{0.693}{10} = 0.0693\ \text{sec}^{-1}$ 　$k_2 = \dfrac{2.303\times 0.3010\times 2}{20}$

　　　　　　　　　　　　　　　$= 0.0693\ \text{sec}^{-1}$

As k_1 and k_2 are equal, hence pseudo rate constant is same.
It follows the pseudo first order reaction.
(ii) Average rate of reaction between 10 to 20 seconds
$= -\Delta[R]\Delta t = -(0.025-0.05)(20-10) = 0.025 10$
$= 0.0025$ mol lit^{-1} sec^{-1}

Ques 50. **(a) For a reaction $A + B \rightarrow P$, the rate is given by Rate $= k[A]\ [B]^2$**
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess?
(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

Ans 50. (a) For the reaction $A + B \rightarrow P$
rate is given by Rate $= k[A]^1[B]^2$
(i) $r_1 = k[A]^1\ [B]^2$
$r_2 = k[A]^1\ [2B]^2 = 4k[A]^1\ [B]^2$
$r_1 = 4r_2$ (rate of reaction becomes 4 times)

(ii) When A is present in large amounts, order w.r.t. A is zero.
Hence overall order = 0 + 2 = 2

(b) $t_{\frac{1}{2}} = \dfrac{0.693}{k}$ $t_{\frac{1}{2}} = 30$ minutes $k = \dfrac{0.693}{30}$ min^{-1}

$k = 0.0231$ min^{-1}

$k = \dfrac{2.303}{t} \log \dfrac{[A_0]}{[A]}$

$t = \dfrac{2.303}{0.0231} \log \dfrac{100}{10}$ $t = \dfrac{2.303}{0.0231}$ min

$\therefore$ $t = \textbf{99.7 min}$

Ques 51. Half-life for a first order reaction 693 s. Calculate the time required for 90% completion of this reaction.

Ans 51.

Using formula :

$t_{1/2} = \dfrac{0.693}{K}$ $\Rightarrow 693\text{ s} = \dfrac{0.693}{K}$

$\therefore$ $K = \dfrac{0.693}{693}$ $\therefore K = 0.001$ s^{-1}

Using formula :

$K = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$ $\Rightarrow t = \dfrac{2.303}{K} \log \dfrac{a}{a-x}$

$\Rightarrow$ $t = \dfrac{2.303}{0.001} \log \dfrac{a}{a-0.9a}$ $\Rightarrow t = \dfrac{2.303}{0.001} \log \dfrac{1}{0.1}$

$\Rightarrow$ $t = 2303 \log 10$ $\Rightarrow t = 2303 \times 1$

$\therefore$ $t = \textbf{2303 s}$