Chemical Kinetics

Recap Notes

- **Chemical kinetics :** It is the branch of chemistry which deals with the study of reaction rates and their mechanisms.
- **Rate of a reaction :** The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time. For the reaction,

  $R \longrightarrow P$, Rate $= -\dfrac{\Delta[R]}{\Delta t}$ or $+\dfrac{\Delta[P]}{\Delta t}$

  Units of rate : Concentration time^{-1} *i.e.*, mol L^{-1} s^{-1} or atm s^{-1} for gaseous reactions.
- **Average rate of reaction :** It is the average value during a large time interval.

  $$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$$
- **Instantaneous rate of reaction :** It is the rate of a reaction at a particular instant of time *i.e.*, when Δt approaches zero.

  $$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$$
- **Factors influencing rate of a reaction :**
  - **Concentration :** Greater the concentrations of the reactants, faster is the rate of reaction.
  - **Physical state of reactants :** Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.
  - **Temperature :** The rate of reaction increases with increase of temperature. For most of the reactions, rate of reaction becomes almost double with 10° C rise of temperature.
  - **Presence of catalyst :** A catalyst generally increases the speed of a reaction.
  - **Surface area of reactants :** For a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.
  - **Presence of light :** Photochemical reactions take place in the presence of light only.
  - **Activation energy :** Lower the activation energy faster is the reaction.
- **Rate law and rate constant :** The equation that correlates the rate of reaction with concentration of reactants is known as *rate law*.
  - For a simple reaction, $A + B \rightarrow C + D$

    Rate $= k[A][B]$ where k is the rate constant which is equal to the rate of reaction when concentration of each of the reactant is unity.
  - For a simple reaction, $aA + bB \rightarrow cC + dD$

    Rate $= k[A]^x[B]^y$ and order of reaction $= x + y$

  Difference between order and molecularity
- **Order and molecularity :**

Molecularity of reaction	Order of reaction
It is the total number of species taking part in a chemical reaction.	It is the sum of the powers of the concentration terms of reacting species in the rate law equation.
It is a theoretical concept.	It is an experimental quantity.

It is derived from the mechanism of reaction.	It is derived from the rate expression.
It can neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer (may range from 0 to 3).
It is applicable only to elementary reactions. The overall molecularity of a complex reaction has no significance.	It is applicable to elementary as well as complex reactions.

- **Half life of reaction :** The time in which the concentration of a reactant is reduced to one half of its initial concentration is called *half life of the reaction*.

  $t_{1/2} \propto \frac{1}{a^{n-1}}$; where n is the order of the reaction.

Rate law, integrated rate law, half-life, units of rate constant and graph for the reactions of different orders :

Order	Rate law	Integrated rate law	Half-life	Units of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L^{-1} s^{-1}	$[A]$ *vs* t; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln [A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ *vs* t; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k\ [A]_0$	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
2	Rate = $k[A]\,[B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	–	L mol^{-1} s^{-1}	–
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol}\,L^{-1})^{1-n}\,s^{-1}$	$\frac{1}{[A]^{n-1}}$ *vs* t; slope = k

- **Pseudo first order reactions :** Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called *pseudo first order reactions. e.g.,*

  ▶ **Acid hydrolysis of ethyl acetate :**

  $$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

  $$\text{Rate} = k'[CH_3COOC_2H_5][H_2O] = k[CH_3COOC_2H_5] \text{ where, } k = k'[H_2O]$$

  ▶ **Acid catalysed inversion of cane sugar :**

  $$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

  $$\text{Rate} = k[C_{12}H_{22}O_{11}]$$

Practice Time

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. The decomposition of dimethyl ether is a fractional order reaction. The rate of reaction is given by rate = $k(p_{CH_3COCH_3})^{3/2}$. If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant respectively?

(a) bar min^{-1}, bar^2 min^{-1}
(b) bar min^{-1}, $bar^{-1/2}$ min^{-1}
(c) $bar^{-1/2}$ min^{-1}, bar^2 min^{-1}
(d) bar min^{-1}, $bar^{1/2}$ min^{-1}

2. The rate of a gaseous reaction is given by the expression $k[A]^2[B]^3$. The volume of the reaction vessel is reduced to one half of the initial volume. What will be the reaction rate as compared to the original rate a?

(a) $\frac{1}{8}a$
(b) $\frac{1}{2}a$
(c) $2a$
(d) $32a$

3. For a reaction $P + Q \rightarrow 2R + S$. Which of the following statements is incorrect?

(a) Rate of disappearance of P = Rate of appearance of S
(b) Rate of disappearance of Q = 2 × Rate of appearance of R
(c) Rate of disappearance of P = Rate of disappearance of Q
(d) Rate of disappearance of Q = $\frac{1}{2}$ × Rate of appearance of R

4. Which of the following statements for order of reaction is not correct?

(a) Order can be determined experimentally.
(b) Order of reaction is equal to the sum of powers of concentration terms in rate law expression.
(c) Order cannot be fractional.
(d) Order is not affected by stoichiometric coefficient of the reactants.

5. The half-life of the reaction $X \rightarrow Y$, following first order kinetics, when the initial concentration of A is 0.01 mol L^{-1} and initial rate is 0.00352 mol L^{-1} min^{-1} will be

(a) 19.69 min
(b) 1.969 min
(c) 7.75 min
(d) 77.5 min

6. The reaction $2X \rightarrow Y + Z$ would be zero order reaction when

(a) rate remains unchanged at any concentration of Y and Z
(b) rate of reaction doubles if concentration of Y is doubled.
(c) rate of reaction remains same at any concentration of X
(d) rate of reaction is directly proportional to square of concentration of X.

7. The rate constant of a first order reaction is 15×10^{-3} s^{-1}. How long will 5.0 g of this reactant take to reduce to 3.0 g?

(a) 34.07 s
(b) 7.57 s
(c) 10.10 s
(d) 15 s

8. The decomposition of a substance follows first order kinetics. If its concentration is reduced to 1/8 of its initial value in 12 minutes, the rate constant of the decomposition system is

(a) $\left(\frac{2.303}{12}\log\frac{1}{8}\right)$ min^{-1}
(b) $\left(\frac{2.303}{12}\log 8\right)$ min^{-1}
(c) $\left(\frac{0.693}{12}\right)$ min^{-1}
(d) $\left(\frac{1}{12}\log 8\right)$ min^{-1}

9. Which of the following statements is not correct?

(a) For a zero order reaction, $t_{1/2}$ is proportional to initial concentration.
(b) For a reaction $t_{1/2} \propto \frac{1}{a^{n-1}}$, where n is order of the reaction.

(c) The unit of rate constant for a reaction is $mol^{1-n} L^{n-1} s^{-1}$ where n is order of the reaction.

(d) The unit of rate of reaction changes with order of reaction.

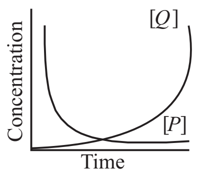
10. Consider the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$. In the reaction NO_2 is being formed at the rate of 0.0125 mol L^{-1} s^{-1}. What is the rate of reaction at this time?

(a) 0.0018 mol L^{-1} s^{-1} (b) 0.0031 mol L^{-1} s^{-1}

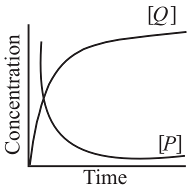
(c) 0.0041 mol L^{-1} s^{-1} (d) 0.050 mol L^{-1} s^{-1}

11. Consider the reaction $P \rightarrow Q$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?

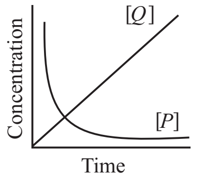
(a)



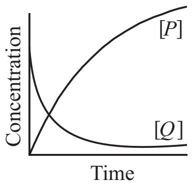
(b)



(c)



(d)



12. The number of molecules of the reactants taking part in a single step of the reaction is indicative of

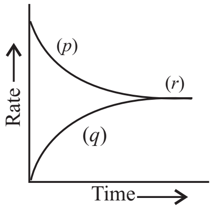
(a) order of a reaction

(b) molecularity of a reaction

(c) fast step of the mechanism of a reaction

(d) half-life of the reaction.

13. For a reversible reaction, $A + B \rightleftharpoons C + D$, the graph for rate of reaction with time is given below.



Mark the terms (p), (q) and (r).

(a) (p) - rate of backward reaction, (q) - rate of forward reaction, (r) - equilibrium

(b) (p) - rate of forward reaction, (q) - rate of backward reaction, (r) - equilibrium

(c) (p) - concentration of products, (q) - concentration of reactants, (r) - rate of reaction

(d) (p) - instantaneous rate of reaction, (q) - variation of rate, (r) - average rate of reaction

14. For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, the rate of reaction can be expressed in terms of time and concentration by the expression:

(a) $\text{Rate} = -\frac{d[N_2O_5]}{dt} = -\frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt}$

(b) $\text{Rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

(c) $\text{Rate} = -\frac{1}{4}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

(d) $\text{Rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt}$

15. In a reaction $2HI \rightarrow H_2 + I_2$, the concentration of HI decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. What is the rate of reaction during this interval?

(a) 5×10^{-3} M min^{-1} (b) 2.5×10^{-3} M min^{-1}

(c) 5×10^{-2} M min^{-1} (d) 2.5×10^{-2} M min^{-1}

16. 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.

17. In pseudo unimolecular reactions,

(a) both the reactants are present in low concentration

(b) both the reactants are present in same concentration

(c) one of the reactants is present in excess

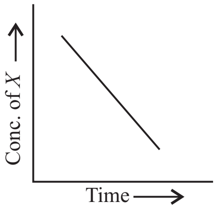
(d) one of the reactants is non-reactive

18. For a reaction $R \rightarrow P$, the concentration of a reactant changes from 0.05 M to 0.04 M in 30 minutes. What will be the average rate of reaction in minutes?

(a) 4×10^{-4} M min^{-1} (b) 8×10^{-4} M min^{-1}

(c) 3.3×10^{-4} M min^{-1} (d) 2.2×10^{-4} M min^{-1}

19. For a general reaction $X \longrightarrow Y$, the plot of conc. of X *vs* time is given in the figure. What is the order of the reaction and what are the units of rate constant?



(a) Zero, mol L^{-1} s^{-1} (b) First, mol L^{-1} s^{-1}
(c) First, s^{-1} (d) Zero, L mol^{-1} s^{-1}

20. Which of the following is an example of a fractional order reaction?
(a) $NH_4NO_2 \rightarrow N_2 + 2H_2O$
(b) $NO + O_3 \rightarrow NO_2 + O_2$
(c) $2NO + Br_2 \rightarrow 2NOBr$
(d) $CH_3CHO \rightarrow CH_4 + CO$

21. The value of rate of a pseudo first order reaction depends upon
(a) the concentration of both the reactants present in the reaction
(b) the concentration of the reactant present in small amount
(c) the concentration of the reactant present in excess
(d) the value of ΔH of the reaction.

22. The rate law for a reaction,
$A + B \rightarrow C + D$ is given by the expression $k[A]$. The rate of reaction will be
(a) doubled on doubling the concentration of B
(b) halved on reducing the concentration of A to half
(c) decreased on increasing the temperature of the reaction
(d) unaffected by any change in concentration or temperature.

23. Nitrogen dioxide (NO_2) dissociates into nitric oxide (NO) and oxygen (O_2) as follows:
$2NO_2 \rightarrow 2NO + O_2$
If the rate of decrease of concentration of NO_2 is 6.0×10^{-12} mol L^{-1} s^{-1}, what will be the rate of increase of concentration of O_2?
(a) 3×10^{-12} mol L^{-1} s^{-1}
(b) 6×10^{-12} mol L^{-1} s^{-1}
(c) 1×10^{-12} mol L^{-1} s^{-1}
(d) 1.5×10^{-12} mol L^{-1} s^{-1}

24. For the reaction $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$, if the rate of disappearance of NH_3 is 3.6×10^{-3} mol L^{-1} s^{-1}, what is the rate of formation of H_2O?
(a) 5.4×10^{-3} mol L^{-1} s^{-1}
(b) 3.6×10^{-3} mol L^{-1} s^{-1}
(c) 4×10^{-4} mol L^{-1} s^{-1}
(d) 0.6×10^{-4} mol L^{-1} s^{-1}

25. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ is 2×10^{-5} s^{-1}. If rate of reaction is 1.4×10^{-5} mol L^{-1} s^{-1}, what will be the concentration of N_2O_5 in mol L^{-1}?
(a) 0.8 (b) 0.7
(c) 1.2 (d) 1

26. When a chemical reaction takes place, during the course of the reaction the rate of reaction
(a) keeps on increasing with time
(b) remains constant with time
(c) keeps on decreasing with time
(d) shows irregular trend with time.

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

28. In a reaction $2X \rightarrow Y$, the concentration of X decreases from 3.0 moles/litre to 2.0 moles/litre in 5 minutes. The rate of reaction is
(a) 0.1 mol L^{-1} min^{-1} (b) 5 mol L^{-1} min^{-1}
(c) 1 mol L^{-1} min^{-1} (d) 0.5 mol L^{-1} min^{-1}

29. The chemical reaction, $2O_3 \rightarrow 3O_2$ proceeds as

$$O_3 \rightleftharpoons O_2 + [O] \qquad \text{(fast)}$$
$$[O] + O_3 \rightarrow 2O_2 \qquad \text{(slow)}$$

The rate law expression will be
(a) Rate $= k[O][O_3]$ (b) Rate $= k[O_3]^2[O_2]^{-1}$
(c) Rate $= k[O_3]^2$ (d) Rate $= k[O_2][O]$

30. Radioactive disintegration is an example of
(a) zero order reaction
(b) first order reaction
(c) second order reaction
(d) third order reaction.

31. In a first order reaction the concentration of reactant decreases from 400 mol L^{-1} to 25 mol L^{-1} in 200 seconds. The rate constant for the reaction is

(a) $1.01386\ s^{-1}$ (b) $2 \times 10^{-4}\ s^{-1}$
(c) $1.386 \times 10^{-2}\ s^{-1}$ (d) $3.4 \times 10^{-4}\ s^{-1}$

32. What will be the rate equation for the reaction $2X + Y \rightarrow Z$, if the order of the reaction is zero?

(a) Rate = $k[X][Y]$ (b) Rate = k
(c) Rate = $k[X]^0[Y]$ (d) Rate = $k[X][Y]^0$

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	0.5
2	100	0.6

What is the rate of reaction when total pressure is 0.65 atm?

(a) $0.35\ atm\ s^{-1}$
(b) $2.235 \times 10^{-3}\ atm\ s^{-1}$
(c) $7.8 \times 10^{-4}\ atm\ s^{-1}$
(d) $1.55 \times 10^{-4}\ atm\ s^{-1}$

34. A first order reaction is 20% complete in 10 minutes. What is the specific rate constant for the reaction?

(a) $0.0970\ min^{-1}$ (b) $0.009\ min^{-1}$
(c) $0.0223\ min^{-1}$ (d) $2.223\ min^{-1}$

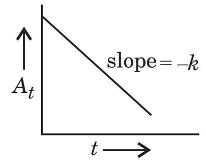
35. In a pseudo first order hydrolysis of ester in water, the following results were obtained.

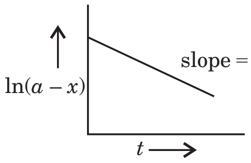
***t*/s**	0	30	60	90
Ester/mol L^{-1}	0.55	0.31	0.17	0.085

What will be the average rate of reaction between the time interval 30 to 60 seconds?

(a) $1.91 \times 10^{-2}\ s^{-1}$
(b) $4.67 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$
(c) $1.98 \times 10^{-3}\ s^{-1}$
(d) $2.07 \times 10^{-2}\ s^{-1}$

36. Two plots are shown below between concentration and time t. Which of the given orders are shown by the graphs respectively?





(a) Zero order and first order
(b) First order and first order
(c) First order and zero order
(d) None of these

37. For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, how are the rate of reaction expressions inter-related $\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$?

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

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

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

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

38. The expression to calculate time required for completion of zero order reaction is

(a) $t = \frac{[R_0]}{k}$ (b) $t = [R] - [R_0]$

(c) $t = \frac{k}{[R_0]}$ (d) $t = \frac{[R_0]-[R]}{[R_0]}$

39. For the reaction $2NH_3 \rightarrow N_2 + 3H_2$, if

$-\frac{d[NH_3]}{dt} = k_1[NH_3]$, $\frac{d[N_2]}{dt} = k_2[NH_3]$,

$\frac{d[H_2]}{dt} = k_3[NH_3]$

then the relation between k_1, k_2 and k_3 is

(a) $k_1 = k_2 = k_3$ (b) $k_1 = 3k_2 = 2k_3$
(c) $1.5k_1 = 3k_2 = k_3$ (d) $2k_1 = k_2 = 3k_3$.

40. The decomposition of dinitrogen pentoxide (N_2O_5) follows first order rate law. What will be the rate constant from the given data?

At $t = 800$ s, $[N_2O_5] = 1.45\ mol\ L^{-1}$
At $t = 1600$ s, $[N_2O_5] = 0.88\ mol\ L^{-1}$

(a) $3.12 \times 10^{-4}\ s^{-1}$ (b) $6.24 \times 10^{-4}\ s^{-1}$
(c) $2.84 \times 10^{-4}\ s^{-1}$ (d) $8.14 \times 10^{-4}\ s^{-1}$

41. 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.

42. Rate of reaction is the change in concentration of any one of the reactants or products per unit time.

For a hypothetical reaction, $A \rightarrow B$

Rate of reaction $= -\dfrac{\Delta[A]}{dt} = \dfrac{\Delta[B]}{dt}$

In a reaction, $A + 2B \rightarrow 3C + 2D$, the concentration of A decreases from 0.5 mol/L to 0.35 mol/L in 15 seconds. Then a student Ajinkya calculated following rates :

I. Rate of formation of C is 0.03 mol/L-s.
II. Rate of formation of D is 0.025 mol/L-s.
III. Rate of disappearance of B is 0.02 mol/L-s.

Which is/are incorrect statement(s)?

(a) I only
(b) II only
(c) II & III both
(d) I & III both

43. For a first order reaction, $[A] = [A]_0 e^{-kt}$ concentration of reactant decreases exponentially with time.

and $t_{1/2} = \dfrac{0.693}{k}$

This relation shows that half-life is independent of concentration and $t_{1/2}$ decreases with the increase of temperature

For first order reaction,

$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

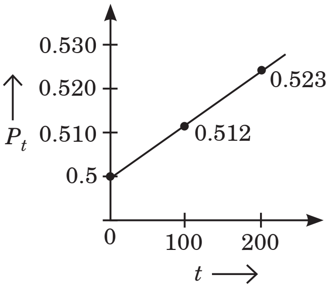
The reaction proceeds to 99.6% completion in

(a) 2 half lives
(b) 6 half lives
(c) 8 half lives
(d) 5 half lives

44. A student of class-12, Jayesh did few experiments for the reaction,

$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$

and he plotted time against total pressure



If this reaction follows first order kinetics, value of rate constant k is

(a) 5.96×10^{-3} s^{-1}
(b) 4.98×10^{-4} s^{-1}
(c) 4.13×10^{-3} s^{-1}
(d) 5.85×10^{-4} s^{-1}

45. Priyanshi after learning chemical kinetics chapter in class, she made notes for zero order and first order reactions as given below:

	Differential Rate law [I]	**Integral Rate law [II]**	**Straight Line plot [III]**	**Half Life [IV]**	**Units [V]**
Zero order	$\dfrac{d[R]}{dt} = -k$	$kt = [R]_0 - [R]$	ln$[R]$ vs t	$[R_o]/k$	mol L^{-1} s^{-1}
First order	$\dfrac{d[R]}{dt} = -k[R]$	$[R] = [R]_0 e^{-kt}$	$[R]$ vs t	ln $2k$	s^{-1}

But the made few mistakes. Identify the wrong listed equations.

(a) Only I and III
(b) Only I and II
(c) Only IV
(d) III and IV

46. For the reaction, $A + B \longrightarrow C$

following data has been observed

From the following data for the reaction between A and B.

Exp. No.	**[A], mol L^{-1}**	**[B], mol L^{-1}**	**initial rate mole L^{-1} s^{-1} at**	
			300 K	**320 K**
I	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
II	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
III	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

The incorrect option about this reaction is

(a) the order of reaction with respect to A is 2
(b) the order of reaction with respect to B is 1
(c) the rate constant for the given reaction is 2.67×10^{5} mol^{-2} L^{2} s^{-1}
(d) none of these.

Case Based MCQs

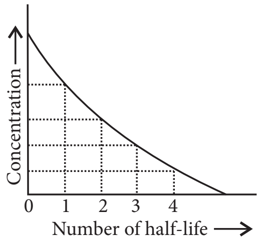
Case I : Read the following and answer the questions from 47 to 51 given below.

The half-life of a reaction is the time required for the concentration of reactant to decrease by half,

i.e., $[A]_t = \dfrac{1}{2}[A]$

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

this means $t_{1/2}$ is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major



portion of the first order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.

47. A first order reaction has a rate constant $k = 3.01 \times 10^{-3}$ /s. How long it will take to decompose half of the reactant?

(a) 2.303 s (b) 23.03 s
(c) 230.3 s (d) 2303 s

48. The rate constant for a first order reaction is $7.0 \times 10^{-4}\ s^{-1}$. If initial concentration of reactant is 0.080 M, what is the half life of reaction?

(a) 990 s (b) 79.2 s
(c) 12375 s (d) 10.10×10^{-4} s

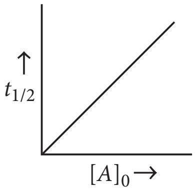
49. For the half-life period of a first order reaction, which one of the following statements is generally false?

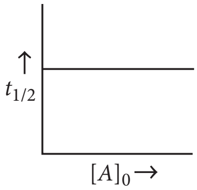
(a) It is independent of initial concentration.
(b) It is dependent on rate of the reaction.
(c) At $t_{1/2}$, the concentration of the reactant is reduced by half.
(d) None of these.

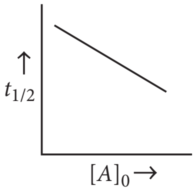
50. The rate of a first order reaction is $0.04\ mol\ L^{-1}\ s^{-1}$ at 10 minutes and $0.03\ mol\ L^{-1}\ s^{-1}$ at 20 minutes after initiation. The half-life of the reaction is

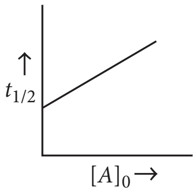
(a) 4.408 min (b) 44.086 min
(c) 24.086 min (d) 2.408 min

51. The plot of $t_{1/2}$ *vs* initial concentration $[A]_0$ for a first order reaction is given by

(a)


(b)


(c)


(d)


Case II : Read the following and answer the questions from 52 to 55 given below.

For a first order reaction, $A \rightarrow$ Products, $k = \frac{2.303}{t}\log\frac{a}{a-x}$, where a is the initial concentration of A and $(a–x)$ is the concentration of A after time t. k is rate constant. Its value is constant at constant temperature for a reaction. The time in which half of the reactant is consumed is called half-life period. Half-life period of a first order reaction is constant. Its value is independent of initial concentration or any other external conditions.

In the following questions (Q. No. 52-55), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

52. Assertion : Rate of reaction doubles when concentration of reactant is doubled if it is a first order reaction.

Reason : Rate constant also doubles.

53. Assertion : For the first order reaction, half-life period is expressed as $t_{1/2} = \frac{2.303}{k}\log 2$.

Reason : The half-life time of a first order reaction is not always constant and it depends upon the initial concentration of reactants.

54. Assertion : For a first order reaction, the concentration of the reactant decreases exponentially with time.

Reason : Rate of reaction at any time depends upon the concentration of the reactant at that time.

55. Assertion : Half-life period for a first order reaction is independent of initial concentration of the reactant.

Reason : For a first order reaction, $t_{1/2} = \frac{0.693}{k}$, where k is rate constant.

Case III : Read the following and answer the questions from 56 to 59 given below.

Number of molecules which must collide simultaneously to give product is called molecularity. It is equal to sum of coefficients of reactants present in stoichiometric chemical equation.

For reaction, $m_1A + m_2B \rightarrow$ Product

Molecularity = $[m_1 + m_2]$

In complex reaction each step has its own molecularity which is equal to the sum of coefficients of reactants present in a particular step. Molecularity is a theoretical property. Its value is any whole number. Number of concentration terms on which rate of reaction depends is called order of reaction or sum of powers of concentration terms present in the rate equation is called order of reaction.

If rate equation of reaction is : $\text{Rate} = k \cdot C_A^{m_1} \cdot C_B^{m_2}$

Then order of reaction = $m_1 + m_2$.

In simple reaction, order and molecularity are same.

In complex reaction, order of slowest step is the order of over all reaction. This step is known as rate determining step. Order is an experimental property. Its value may be zero, fractional or negative.

56. The rate of reaction, $A + 2B \rightarrow$ products, is given by the following equation: $-\frac{d[A]}{dt} = k[A][B]^2$

If B is present in large excess, the order of the reaction is

(a) zero (b) first
(c) second (d) third.

57. The molecularity of the reaction :

$6FeSO_4 + 3H_2SO_4 + KClO_3 \rightarrow$
$KCl + 3Fe_2(SO_4)_3 + 3H_2O$ is

(a) 6 (b) 3
(c) 10 (d) 7

58. Which of the following statements is false in the following?

(a) Order of a reaction may be even zero.
(b) Molecularity of a reaction is always a whole number.
(c) Molecularity and order always have same values for a reaction.
(d) Order of a reaction depends upon the mechanism of the reaction.

59. The rate of the reaction, $A + B + C \rightarrow$ products, is given by $r = -\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$. The order of the reaction is

(a) $\frac{1}{3}$ (b) $\frac{1}{4}$ (c) $\frac{1}{2}$ (d) $\frac{13}{12}$

Case IV : Read the following and answer the questions from 60 to 64 given below.

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 disapp. 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	?

60. The molecularity of the reaction is

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

61. The expression for rate law is

(a) $r = k[NO][Cl_2]$ (b) $r = k[NO]^2[Cl_2]$
(c) $r = k[NO][Cl_2]^2$ (d) $r = k[NO]^2[Cl_2]^2$

62. The overall order of the reaction is

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

63. The value of rate constant is

(a) 150.32 M^{-2} min^{-1} (b) 200.08 M^{-1} min^{-1}
(c) 177.77 M^{-2} min^{-1} (d) 155.75 M^{-1} min^{-1}

64. The initial rate of disappearance of Cl_2 in experiment 4 is

(a) 1.75 M min^{-1} (b) 3.23 M min^{-1}
(c) 2.25 M min^{-1} (d) 2.77 M min^{-1}

Case V : Read the following and answer the questions from 65 to 69 given below.

A reaction is said to be of the first order if the rate of the reaction depends upon one concentration term only. For a first order reaction of the type $A \rightarrow$ Products, the rate of the reaction is given as : rate = $k[A]$. The differential rate law is given as :

$\frac{dA}{dt} = -k[A]$. The integrated rate law is :

$\ln \frac{[A]}{[A]_0} = -kt$, where $[A]$ is the concentration of reactant left at time t and $[A]_0$ is the initial concentration of the reactant, k is the rate constant.

65. The unit of rate constant for a first order reaction is

(a) s^{-1} (b) mol L^{-1} s^{-1}
(c) L mol^{-1} s^{-1} (d) L^2 mol^{-2} s^{-1}

66. Half-life period of a first order reaction is 10 min. Starting with initial concentration 12 M, the rate after 20 min is

(a) 0.693×3 M min^{-1} (b) 0.0693×4 M min^{-1}

(c) 0.0693 M min^{-1} (d) 0.0693×3 M min^{-1}

67. 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

(a) 70.4 minutes (b) 76.4 minutes

(c) 38.7 minutes (d) 35.2 minutes

68. For a first order reaction, $(A) \rightarrow$ products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M, is

(a) 3.47×10^{-4} M/min (b) 3.47×10^{-5} M/min

(c) 1.73×10^{-4} M/min (d) 1.73×10^{-5} M/min

69. The half-life period of a 1st order reaction is 60 minutes. What percentage will be left over after 240 minutes?

(a) 6.25% (b) 4.25%

(c) 5% (d) 6%

Assertion & Reasoning Based MCQs

For question numbers 70-80, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

70. Assertion : The rate of the reaction is the rate of change of concentration of a reactant or a product.

Reason : Rate of reaction remains constant during the complete reaction.

71. Assertion : The rate law equation can be found only by experiment.

Reason : It can be written from stoichiometric equation.

72. Assertion : The order of the reaction

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

is 1.

Reason : The molecularity of this reaction is 2.

73. Assertion : For the reaction,

$2N_2O_5 \rightarrow 4NO_2 + O_2$, Rate $= k[N_2O_5]$

Reason : Rate of decomposition of N_2O_5 is determined by slow step.

74. Assertion : Half-life period of a reaction of first order is independent of initial concentration.

Reason : The time taken for completion of 75% of a first order reaction is equivalent to two half lives.

75. Assertion : Chemical kinetics deals with the rate of reaction, the factors affecting the rate of the reaction and the mechanism by which the reaction proceeds.

Reason : Nature of reactants, concentration of reactants, products and catalyst affect the rate of reaction.

76. Assertion : Formation of HI is a bimolecular reaction.

Reason : Two molecules of reactants are involved in this reaction.

77. Assertion : Hydrolysis of cane sugar is a pseudo first order reaction.

Reason : Water is present in large excess during hydrolysis.

78. Assertion : Rate of reaction can be expressed as rate of change in partial pressure of the gaseous reactants or products.

Reason : Partial pressure of a gas is equal to its concentration.

79. Assertion : The decomposition of NH_3 on finely divided platinum surface is first order when the concentration is low, however at higher concentration, the reaction becomes zero order.

Reason : In first order reaction, the rate of reaction is proportional to the first power of the concentration of the reactant.

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

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

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. Distinguish between molecularity and order of a reaction.

2. Define the half-life period of reaction ($t_{½}$).

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

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

5. Draw a graph between concentration and time for a zero order reaction.

6. Express the rate of the following reaction in terms of the formation of ammonia.

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

7. If the rate constant of reaction is $k = 3 \times 10^{-4} s^{-1}$, then identify the order of the reaction.

8. For the reaction $3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$, how are the rate of reaction $\frac{-d[H_2]}{dt}$ expression and $\frac{d[NH_3]}{dt}$ interrelated?

9. Define elementary step in a reaction.

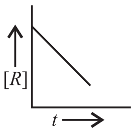
10. Distinguish between 'rate expression' and 'rate constant' of a reaction.

Short Answer Type Questions (SA-I)

11. 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?

12. 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?

13. For a reaction

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

the proposed mechanism is as given below :

(1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

(2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(i) Write rate law for the reaction.

(ii) Write the overall order of reaction.

(iii) Out of steps (1) and (2), which one is rate determining step?

14. For a first order reaction, the time taken to reduce initial concentration by a factor of 1/4 is 10 minutes. What will be the time required to reduce initial concentration by a factor of 1/16?

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

16. What is meant by rate of reaction? Differentiate between average rate and instantaneous rate of reaction.

17. For a reaction $A + B \longrightarrow P$, 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?

18. 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-fourth of initial quantity of HCO_2H to decompose.

(log 0.25 = – 0.6021)

19. For a reaction : $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$; Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

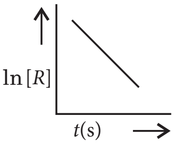
20. For the reaction, $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$, the rate of formation of $NO_{2(g)}$ is 2.8×10^{-3} M s^{-1}. Calculate the rate of disappearance of $N_2O_{5(g)}$.

Short Answer Type Questions (SA-II)

21. What do you understand by the 'order of a reaction'? Identify the reaction order from each of the following units of reaction rate constant :

(i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1}

22. For a chemical reaction $R \longrightarrow P$, the variation in the concentration, ln [R] *vs*. time (s) plot is given as



(i) Predict the order of the reaction.

(ii) What is the slope of the curve?

(iii) Write the unit of the rate constant for this reaction.

23. For a reaction, the rate law is :
Rate = k [A][B]$^{1/2}$. Can this reaction be an elementary reaction?

24. 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?

(iv) What is molecularity of a reaction?

25. In a pseudo first order hyrolysis of ester in water, the following results are obtained :

***t* in seconds**	0	30	60	90
[Ester]M	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

26. The rate of decomposition of ammonia is found to depend upon the concentration of NH_3 according to the equation $-\frac{d[NH_3]}{dt} = \frac{k_1[NH_3]}{1+k_2[NH_3]}$

What will be the order of reaction when

(i) concentration of NH_3 is very high?

(ii) concentration of NH_3 is very low?

27. A certain reaction takes 5 minutes for initial concentration 0.5 mol L^{-1} to become 0.25 mol L^{-1} and another 5 minutes to becomes 0.125 mol L^{-1}. What is the order and specific rate constant of the reaction?

28. Following data are obtained for the reaction :

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

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)

29. A first order reaction takes 160 minutes time for 20% completion. Calculate time required for half completion of reaction.

30. 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 $k = 1.06 \times 10^{-3}$ 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?

31. When inversion of sucrose is studied at pH = 5, the half-life period is always found to be 500 minutes irrespective of any initial concentration but when it is studied at pH = 6, the half-life period is found to be 50 minutes. Derive the rate law expression for the inversion of sucrose.

32. What will be the rate of decomposition of N_2O_5 and rate of formation of NO_2 and O_2 when [N_2O_5] = 0.40 M for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$. The rate constant for this reaction is 3.1×10^{-4} min^{-1}.

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

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

Experiment	**Time/s**	**Total pressure/atm**
1	0	0.4
2	100	0.7

Calculate the rate constant.

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

34. From the data given below, calculate order of reaction.

S.No.	[*A*](M)	[*B*](M)	Rate (M s^{-1})
1.	1.0	0.20	0.10
2.	2.0	0.20	0.20
3.	2.0	0.40	0.80

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

$$C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$$

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)

Long Answer Type Questions (LA)

36. Calculate the order of the reaction and the rate constant for the decomposition of N_2O_5 at 30°C from the following rate data.

S.No.	Rate of reaction (Mol L^{-1} hr^{-1})	Concentration of N_2O_5 (Mol L^{-1})
1.	0.10	0.34
2.	0.20	0.68
3.	0.40	1.36

37. The half-life period of a first order reaction is 30 minutes. Calculate the specific reaction rate of the reaction. What fraction of the reactant remains after 70 minutes?

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

t/s	0	30	60
[CH_3COOCH_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)

39. For a homogeneous gas phase reaction $A_{(g)} \rightarrow B_{(g)} + C_{(g)} + D_{(g)}$, the pressure of the reaction mixture increases by 40% in 20 minute. Calculate rate constant of a reaction.

40. The following results have been obtained during the kinetic studies of the reaction :

$$2A + B \longrightarrow C + D$$

Experiment No.	[*A*]	[*B*]	Initial rate of formation of *D*
1.	0.1 M	0.1 M	6.0×10^{-3} M min^{-1}
2.	0.3 M	0.2 M	7.2×10^{-2} M min^{-1}
3.	0.3 M	0.4 M	2.88×10^{-1} M min^{-1}
4.	0.4 M	0.1 M	2.40×10^{-2} M min^{-1}

Calculate the rate of formation of *D* when [*A*] = 0.5 mol L^{-1} and [*B*] = 0.2 mol L^{-1}.

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. **(b) :** In terms of pressure, Rate = $k(p_{CH_3COCH_3})^{3/2}$

Units of rate = bar min^{-1}

$$\text{Units of rate constant} = \frac{\text{rate}}{(p_{CH_3OCH_3})^{3/2}}$$

$$= \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2}\ \text{min}^{-1}$$

2. **(d) :** Rate = $k[A]^2\,[B]^3 = a$

When volume is reduced to one half then conc. of reactants will be doubled.

Rate = $k[2A]^2\,[2B]^3 = 32\,k[A]^2\,[B]^3 = 32a$

3. **(b) :** Rate of disappearance of $Q = \frac{1}{2}$ × rate of appearance of *R*

4. **(c) :** Order of reaction can be zero, fractional or negative.

5. (b) : $\frac{dx}{dt} = k[X]$ (For a first order reaction)

$0.00352 = k \times 0.01 \Rightarrow k = 0.352$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.352} = 1.969 \text{ min}$$

6. (c) : Rate of a zero order reaction is independent of the concentration of reactants.

7. (a) : $t = \frac{2.303}{k}\log\left(\frac{a}{a-x}\right)$ or $t = \frac{2.303}{15\times10^{-3}}\log\left(\frac{5}{3}\right) = 34.07$ s

8. (b) : $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$ (for first order)

$$k = \frac{2.303}{12}\log\frac{1}{1/8} = \left(\frac{2.303}{12}\log 8\right) \text{ min}^{-1}$$

9. (d) : The unit of rate of reaction is mol L^{-1} s^{-1}. It does not change with order.

10. (b) : $\text{Rate} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{4}\times 0.0125 = 0.0031 \text{ mol L}^{-1}\text{ s}^{-1}$

11. (b) : In a reaction $P \rightarrow Q$, concentration of reactant decreases as concentration of product increases during the course of a reaction.

12. (b) : The number of molecules of the reactants taking part in a single step of the reaction tells about molecularity of the reaction.

13. (b) : Rate of forward reaction decreases and rate of backward reaction increases with passage of time. At equilibrium both the rates become equal.

14. (b) : For $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate of reaction can be expressed as

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

15. (a) : Average rate $= -\frac{1}{2}\frac{\Delta[R]}{\Delta t} = -\frac{1}{2}\times\frac{0.4-0.5}{10}$

$$= \frac{1}{2}\times\frac{0.1}{10} = 5\times10^{-3} \text{ M min}^{-1}$$

16. (a) : For a zero order reaction, rate = $k[A]^0 = k$

Units = mol L^{-1} s^{-1}

17. (c) : When one of the reactants is in excess the reaction behaves as a first order reaction.

18. (c) : Average rate $= -\frac{\Delta[R]}{\Delta t} = -\frac{([R]_2 - [R]_1)}{t_2 - t_1}$

$$= -\frac{(0.04-0.05)}{30} = \frac{0.01}{30} = 3.3\times10^{-4} \text{ M min}^{-1}$$

19. (a) : For a zero order reaction, rate = $k = \frac{dx}{dt}$

Units of k = mol L^{-1} s^{-1}

20. (d) : $CH_3CHO \rightarrow CH_4 + CO$

Rate = $k[CH_3CHO]^{3/2}$

21. (b) : If one of the reactant is present in excess, the reaction becomes independent of the concentration of that reactant hence it becomes pseudo first order reaction.

Thus, rate of pseudo first order reaction depends upon the concentration of the reactant present in small amount.

22. (b) : The rate of reaction depends upon concentration of only A.

23. (a) : For the reaction, $2NO_2 \rightarrow 2NO + O_2$

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$$

$$-\frac{d[NO_2]}{dt} = 6\times10^{-12} \text{ mol L}^{-1}\text{ s}^{-1}$$

$$\frac{d[O_2]}{dt} = 3\times10^{-12} \text{ mol L}^{-1}\text{ s}^{-1}$$

24. (a) : $-\frac{1}{4}\frac{d[NH_3]}{dt} = +\frac{1}{6}\frac{d[H_2O]}{dt}$

$$\frac{d[H_2O]}{dt} = \frac{6}{4}\times3.6\times10^{-3} = 5.4\times10^{-3} \text{ mol L}^{-1}\text{ s}^{-1}$$

25. (b) : Rate = $k[N_2O_5]$ (first order as unit of rate constant is s^{-1})

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{1.4\times10^{-5} \text{ mol L}^{-1}\text{ s}^{-1}}{2\times10^{-5}\text{ s}^{-1}} = 0.7 \text{ mol L}^{-1}$$

26. (c) : Rate of reaction ∝ conc. of reactants

As the reaction proceeds, concentration of the reactants decreases hence the rate also keeps on decreasing with time.

27. (a) : For a unimolecular reaction, both order and molecularity are one in rate determining step.

28. (a) : $\text{Rate} = -\frac{1}{2}\frac{\Delta[X]}{\Delta t} = -\frac{1}{2}\frac{(2-3)}{5} = -0.1 \text{ mol L}^{-1}\text{ min}^{-1}$

29. (b) : $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + [O]$ (fast)

$[O] + O_3 \xrightarrow{k_2} 2O_2$ (slow)

Rate of reaction is determined by slow step hence,

Rate = $k_2[O][O_3]$

[O] is unstable intermediate so substitute the value of [O] in above equation.

Rate of forward reaction = $k_1[O_3]$

Rate of backward reaction = $k_{-1}[O_2][O]$

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$k_1[O_3] = k_{-1}[O_2][O]$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

Rate = $k_2\left(\frac{k_1[O_3]}{k_{-1}[O_2]}\right)[O_3]$; Rate = $\frac{k[O_3]^2}{[O_2]}$

30. (b) : Radioactive disintegration is an example of first order reaction.

$$k = \frac{2.303}{t}\log\left(\frac{N_0}{N_t}\right)$$

31. (c) : For first order reaction,

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) = \frac{2.303}{200}\log\left(\frac{400}{25}\right)$$

$$= \frac{2.303}{200} \times 1.204 = 0.01386\ \text{s}^{-1} = 1.386 \times 10^{-2}\ \text{s}^{-1}$$

32. (b) : Rate = $k[X]^0\ [Y]^0$ or rate = k

33. (c) :

$$\begin{array}{lccc} & SO_2Cl_2 \rightarrow & SO_2 + & Cl_2 \\ \text{Initial pressure} & p_0 & 0 & 0 \\ \text{Pressure at time } t & p_0 - p & p & p \end{array}$$

Let initial pressure $p_0 \propto R_0$

Pressure at time t, $P_t = p_0 - p + p + p = p_0 + p$

Pressure of reactants at time t, $p_0 - p = 2p_0 - P_t \propto R$

$$k = \frac{2.303}{t}\log\left(\frac{p_0}{2p_0 - P_t}\right)$$

$$= \frac{2.303}{100}\log\left(\frac{0.5}{2 \times 0.5 - 0.6}\right) = \frac{2.303}{100}\log 1.25$$

= $2.2318 \times 10^{-3}\ \text{s}^{-1}$

Pressure of SO_2Cl_2 at time t ($p_{SO_2Cl_2}$)

= $2p_0 - P_t = 2 \times 0.50 - 0.65$ atm = 0.35 atm

Rate at that time = $k \times p_{SO_2Cl_2}$

= $(2.2318 \times 10^{-3}) \times (0.35) = 7.8 \times 10^{-4}$ atm s^{-1}

34. (c) : $a - x = \frac{80}{100} \times a = 0.8a$, t = 10 min

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) = \frac{2.303}{10}\log\left(\frac{a}{0.8a}\right)$$

$$k = 0.2303 \log\frac{10}{8} = 0.2303(1 - 0.9030)$$

$$= 0.2303 \times 0.0970 = 0.0223\ \text{min}^{-1}$$

35. (b) : Average rate during the time interval 30-60 s.

$$\text{Rate} = -\frac{C_2 - C_1}{t_2 - t_1} = -\frac{(0.17 - 0.31)}{60 - 30} = \frac{0.14}{30}$$

$$= 4.67 \times 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

36. (a) : Linear plots are obtained in the graph of A_t *vs* t for zero order reaction and ln $a - x$ *vs* t for first order reaction.

37. (a) : For the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$,

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

38. (a) : $[R] = [R]_0 - kt$

For completion of reaction $[R] = 0$

or $t = \frac{[R]_0}{k}$

39. (c) : $2NH_3 \longrightarrow N_2 + 3H_2$

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

$$\frac{1}{2}k_1[NH_3] = k_2[NH_3] = \frac{1}{3}k_3[NH_3]$$

$$1.5k_1 = 3k_2 = k_3$$

40. (b) : $k = \frac{2.303}{(t_2 - t_1)}\log\frac{[A_1]}{[A_2]}$

$$k = \frac{2.303}{(1600 - 800)}\log\frac{1.45}{0.88} = \frac{2.303}{800} \times 0.2169$$

$$= 6.24 \times 10^{-4}\ \text{s}^{-1}$$

41. (d) : The slowest step is rate determining step.

42. (b) : $\frac{1}{3}\frac{[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt} = \frac{-d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$

$$= \frac{-d[A]}{dt} = -\frac{(0.035 - 0.5)}{15} = \frac{0.15}{15} = 0.01\ \text{mol/L-s}$$

$$\frac{-d[B]}{dt} = 0.02\ \text{mol/L-s}$$

$$\frac{d[C]}{dt} = 3 \times 0.01 = 0.03\ \text{mol/L-s}$$

$$\frac{d[D]}{dt} = 2 \times 0.01 = 0.02\ \text{mol/L-s}$$

43. (c) : For 99.6% completion,

Let a = 100 x = 99.6 $a - x$ = 0.4

$$k = \frac{2.303}{t_{99.6}}\log\frac{100}{0.4} = \frac{2.303}{t_{99.6}}\log 250$$

$$t_{99.6\%} = \frac{2.303}{k}\log 250 \qquad \text{...(i)}$$

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

From equation (i) & (ii)

$$t_{99.6\%} = \frac{2.303}{0.693} \times 2.4 \times t_{1/2} = 8t_{1/2}$$

44. (b) : The following data were obtained during the first order thermal decomposition of $N_2O_{5(g)}$ at constant volume :

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Let the pressure of $N_2O_{5(g)}$ decrease by 2x 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 $2x$ atm and that of $O_{2(g)}$ increases by x atm.

	$2N_2O_{4(g)} \longrightarrow$	$2N_2O_{4(g)}$ +	$O_{2(g)}$
Start $t = 0$	0.5 atm	0 atm	0 atm
At time t	$(0.5 - 2x)$ atm	$2x$ atm	x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$
$$= (0.5 - 2x) + 2x + x = 0.5 + x$$
$$x = p_t - 0.5$$
$$p_{N_2O_5} = 0.5 - 2x$$
$$= 0.5 - 2\,(p_t - 0.5) = 1.5 - 2p_t$$

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

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

We know that,

$$k = \frac{2.303}{t}\log\frac{p_{t=0}}{p_{t=100}} = \frac{2.303}{100}\log\frac{0.5\text{ atm}}{0.476\text{ atm}}$$
$$= \frac{2.303}{100} \times 0.0216 = 4.98 \times 10^{-4}\ \text{s}^{-1}$$

45. (d) : For zero order reaction,

$[R]$ *vs* t is a straight line plot and half life $t_{1/2} = \frac{[R]_0}{2k}$.

For first order reaction ln $[R]$ *vs* t gives straight line plot and half life = $\frac{\ln 2}{k}$

46. (c) : (i) Rate law can be written as follows:

Rate = $k[A]^p\,[B]^q$

From experiments I, II and III

$(\text{Rate})_1 = k[2.5 \times 10^{-4}]^p\,[3.0 \times 10^{-5}]^q = 5.0 \times 10^{-4}$ ...(i)

$(\text{Rate})_2 = k[5.0 \times 10^{-4}]^p\,[6.0 \times 10^{-5}]^q = 4.0 \times 10^{-3}$ ...(ii)

$(\text{Rate})_3 = k[1.0 \times 10^{-3}]^p\,[6.0 \times 10^{-5}]^q = 1.6 \times 10^{-2}$ ...(iii)

Dividing equation (iii) by equation (ii),

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{(1.0 \times 10^{-3})^p}{(5.0 \times 10^{-4})^p} = \frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}}$$

or $2^p = 4$ or $2^p = 2^2$ *i. e.* $p = 2$

Dividing equation (ii) by equation (i),

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{(5.0 \times 10^{-4})^p\,(6.0 \times 10^{-5})^q}{(2.5 \times 10^{-4})^p\,(3.0 \times 10^{-5})^q} = \frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}}$$

or $2^p.\,2^q = 8$ or $2^2.\,2^q = 8$

or $2^q = 8/2^2$ or $2^q = 2^1$ or $q = 1$

Thus the rate equation is Rate = $k[A]^2\,[B]$

$\therefore$ Order of reaction with respect to $A = 2$

Order of reaction with respect to $B = 1$

(ii) Rate constant (k) at 300 K :

From experiment 1, we have

Rate = $k(2.5 \times 10^{-4})^2\,(3.0 \times 10^{-5})$

or 5.0×10^{-4} mol L^{-1}

$= k(2.5 \times 10^{-4}\ \text{mol L}^{-1})^2\,(3.0 \times 10^{-5}\ \text{mol L}^{-1})$

$$\text{or } k = \frac{5.0 \times 10^{-4}\,(\text{mol L}^{-1})^3}{(2.5 \times 10^{-4})^2\,(3.0 \times 10^{-5})}$$
$$= 2.67 \times 10^8\ \text{mol}^{-2}\,\text{L}^2\,\text{s}^{-1}$$

47. (c) : For a first order reaction :

$$t_{1/2} = \frac{0.693}{k},\quad k = 3.01 \times 10^{-3}\ \text{s}^{-1}$$
$$\therefore \quad t_{1/2} = \frac{0.693}{3.01 \times 10^{-3}} = 230.3\ \text{s}$$

48. (a) : Half life ($t_{1/2}$) of a first order reaction is given as :

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.0 \times 10^{-4}} = 990\ \text{s}$$

49. (b) : For a first order reaction $t_{1/2} = \frac{0.693}{k}$

therefore $t_{1/2}$ depends solely on k.

50. (c) : Let the concentrations of the reactant after 10 min and 20 min be C_1 and C_2 respectively.

$\therefore$ Rate after 10 min = 0.04×60 mol L^{-1}min^{-1} = $k.C_1$

and rate after 20 min = 0.03×60 mol L^{-1}min^{-1} = $k.C_2$

$$\therefore \quad \frac{C_1}{C_2} = \frac{0.04 \times 60}{0.03 \times 60} = \frac{4}{3}$$

Let the reaction starts after 10 minutes.

$$k = \frac{2.303}{10}\log\frac{C_1}{C_2} = \frac{2.303}{10}\log\frac{4}{3} = 0.02878$$
$$\therefore \quad t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{0.02878} = 24.086\ \text{min}$$

51. (b) : For a first order reactions, $t_{1/2} = k[A]_0^0 = k$. Thus $t_{1/2}$ is independent of initial concentration. Hence plot of $t_{1/2}$ *vs* $[A]_0$ will be a horizontal line.

52. (c) : For first order reaction, $\text{Rate}_1 = k[A_1]$
According to question, $[A_2] = [2A_1]$
$\therefore \quad \text{Rate}_2 = k[2A_1] \Rightarrow \text{Rate}_2 = 2\ \text{Rate}_1$
For a given reaction, rate constant is constant and independent of the concentration of reactant.

53. (c) : For a first order reaction $k = \frac{2.303}{t}\log\frac{a}{a-x}$

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

Therefore half-life period $t_{1/2} = \frac{2.303}{k}\log 2.$

Thus $t_{1/2}$ is independent of initial concentration of reactant for first order reaction.

54. (b) : For a first order reaction, $[A] = [A]_0 e^{-kt}$ ...(i)
According to eq. (i), concentration of reactant decreases exponentially.

55. (a) : For a first order reaction, $t_{1/2}$ is inversely proportional to k, it does not depend on the initial concentration of the reactant.

56. (b) : From the expression

$$-\frac{d[A]}{dt} = k[A][B]^2$$

when B is present in large excess, rate will be independent upon the change in conc. of B, therefore order of reaction will be one.

57. (c) : The total number of reactant molecules participating in a chemical reaction is known as its molecularity, hence the molecularity = 6 + 3 + 1 = 10.

58. (c) : Molecularity may or may not be equal to the order of a reaction.

59. (d) : Order of reaction $= \frac{1}{2}+\frac{1}{3}+\frac{1}{4} = \frac{6+4+3}{12} = \frac{13}{12}$

60. (c) : $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$
Molecularity = 3

61. (b) : Let the rate of this reaction, $r = k[NO]^m[Cl_2]^n$

then $\frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$

or, $\frac{1}{2} = \left(\frac{1}{2}\right)^n \quad \Rightarrow \quad n = 1$

Again from $\frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^n}{k(0.30)^m(0.15)^n}$

or $\quad \frac{1}{2} = \left(\frac{1}{2}\right)^m \cdot \frac{2}{1}$ or $\frac{1}{4} = \left(\frac{1}{2}\right)^m \quad \Rightarrow \quad m = 2$

Hence, expression for rate law is
$r = k[NO]^2\ [Cl_2]^1$

62. (d) : As the order *w.r.t.* NO is 2 and order *w.r.t.* Cl_2 is 1, hence the overall order is 3.

63. (c) : Substituting the values of experiment 1 in rate law expression
$0.60\ \text{M min}^{-1} = k(0.15\ \text{M})^2\ (0.15\ \text{M})^1$

or $k = \frac{0.60\ \text{M min}^{-1}}{0.0225 \times 0.15\ \text{M}^3} = 177.77\ \text{M}^{-2}\ \text{min}^{-1}$

64. (d) : $r = 177.7\ \text{M}^{-2}\ \text{min}^{-1} \times (0.25\ \text{M})^2\ (0.25\ \text{M})$
$= 2.77\ \text{M min}^{-1}$

65. (a) : Unit of rate constant for a reaction of n^{th} order = $(\text{conc.})^{1-n}\ \text{time}^{-1}$
For a first order reaction, $n = 1$
Unit of rate constant = $(\text{mol L}^{-1})^{1-1}\ \text{s}^{-1} = \text{s}^{-1}$

66. (d) : $\underset{\text{Initial conc.}}{12\,\text{M}} \xrightarrow{t_{1/2}} 6\,\text{M} \xrightarrow{t_{1/2}} 3\,\text{M}$

$t_{1/2} = 10$ min

$k = \frac{0.693}{10} = 0.0693\ \text{min}^{-1}$

As $t_{1/2}$ is 10 min, after 20 minutes the concentration will be 3 M.
Hence, Rate = $0.0693 \times 3\ \text{M min}^{-1}$

67. (b) : $t_{1/2}$ = 23 minutes

$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{1/2}} \Rightarrow k = \frac{0.693}{23}\ \text{min}^{-1}$

For 90% completion,

$t = \frac{2.303}{k}\log\left(\frac{a}{a-x}\right);\ t = \frac{2.303 \times 23}{0.693}\log\left(\frac{100}{100-90}\right)$

t = 76.4 minutes

68. (a) : For the first order reaction, $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

$a = 0.1$ M, $a - x = 0.025$ M, $t = 40$ min

$k = \frac{2.303}{40}\log\frac{0.1}{0.025} = \frac{2.303}{40}\log 4 = 0.0347\ \text{min}^{-1}$
$[A] \rightarrow$ product
Thus, rate = $k[A]$
rate = $0.0347 \times 0.01\ \text{M min}^{-1} = 3.47 \times 10^{-4}\ \text{M min}^{-1}$

69. (a) : $t_{1/2} = \frac{0.693}{k} \Rightarrow \frac{0.693}{t_{1/2}} = k \Rightarrow \frac{0.693}{60} = k$

$k = 0.01155\ \text{min}^{-1}$

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

Let the initial amount (a) be 100.

$0.01155\ \text{min}^{-1} = \frac{2.303}{240\,\text{min}}\log\left(\frac{100}{a-x}\right)$

$$\frac{0.01155\,\text{min}^{-1}\times 240\,\text{min}}{2.303}=\log\left(\frac{100}{a-x}\right)$$

$1.204 = \log 100 - \log (a - x)$

$1.204 = 2 - \log (a - x)$

$\log (a - x) = 2 - 1.204 = 0.796$

$(a - x) = 6.25\%$

70. (c) : Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.

71. (c) : The rate law equation cannot be written from stoichiometric equation.

72. (b) : During hydrolysis of ester, water is always present in high concentration, thus there is very little change in its concentration and it practically remains constant. Thus, the order of reaction is 1 (pseudo first order reaction).

73. (a) : Rate of any reaction is equal to the rate of its slowest step and here rate of given reaction = $k\,[N_2O_5]$ because the slowest step has only N_2O_5 molecule involved.

74. (b)

75. (b)

76. (a) : A bimolecular reaction may involve combination of two molecules or exchange of atoms or groups of atoms between the two reactant molecules.

77. (a) : Hydrolysis of cane sugar is pseudo first order reaction. Since, water is always in excess, rate of reaction does not depend appreciably on its concentration, thus it is an example of pseudo unimolecular reactions.

78. (c) : For a gaseous reaction at constant T, concentration is directly proportional to the partial pressure of the species. Thus, the rate of reaction can be expressed in terms of partial pressure for gaseous reactants or products.

79. (b) : In a heterogeneous system, the reactant is absorbed on the surface of a solid catalyst. The fraction of the surface of the catalyst covered by the reactant is proportional to its concentration at low values and the rate of reaction is first order. However at higher concentration, the surface of catalyst is fully covered and the reaction rate becomes independent of concentration and it becomes zero order reaction.

80. (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.

SUBJECTIVE TYPE QUESTIONS

1.

	Order of a reaction		Molecularity of a reaction
1.	It is the sum of powers of the concentration of the reactants in the rate law expression.	1.	It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2.	It can be zero or even a fraction.	2.	It is always a whole number.

Generally, in a complex reaction the order of reaction is equal to the molecularity of the slowest step.

2. The time taken for half of the reaction to complete, i.e., the time in which the concentration of a reactant is reduced to half of its original value is called half-life period of the reaction.

$t = t_{1/2}$ when $[R] = \dfrac{[R_0]}{2}$

3. Half-life of first order reaction is independent of the initial concentration of reactants.

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

4. For a first order reaction, $k=\dfrac{0.693}{t_{1/2}}=\dfrac{0.693}{x}$

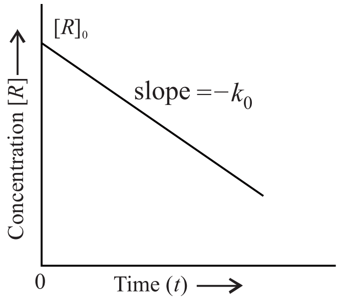
For $\dfrac{3}{4}$th life period, $a-x=a-\dfrac{3}{4}a=\dfrac{1}{4}a$

$\therefore \quad k=\dfrac{2.303}{y}\log\dfrac{a}{(a-x)}\,;\quad \dfrac{0.693}{x}=\dfrac{2.303}{y}\log\dfrac{a}{a/4}$

$\dfrac{0.693}{x}=\dfrac{2.303}{y}2\log 2\,;\quad \dfrac{0.693}{x}=\dfrac{0.693\times 2}{y}$

$y = 2x$

5. $[R] = -k_0t + [R]_0$



6. $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

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

7. First order reaction has s^{-1} as the unit of the rate constant.

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

9. Elementary step : Each step of a complex reaction is called an elementary step.

10. Rate expression is a way of expressing rate of reaction in terms of concentration of reactants, *e.g.*, for a general reaction, $aA + bB \longrightarrow cC + dD$

$$\text{Rate} = k[A]^x [B]^y$$

Rate constant (k) is equal to the rate of reaction when molar concentration of reactant is unity. Its units depends upon the order of reaction.

11. Rate law, $r = k[A]^{1/2} [B]^2$

Order of reaction is sum of the powers of concentration terms,

$$\therefore \quad \text{Order of reaction } = \frac{1}{2}+2=\frac{5}{2}=2.5$$

12. (i) The reaction is of zero order.

(ii) Slope of the curve $= -k = \dfrac{d[R]}{dt}$

13. (i) Rate = $k[H_2O_2][I^-]$

(ii) Overall order of reaction is 2.

(iii) Step (1) being the slow step is the rate determining step of the reaction.

14. Let initial concentration (a) = 1

then, final concentration ($a - x$) = 1/4

$$\therefore \quad t_{1/4}=\frac{2.303}{k}\log\frac{1}{1/4} \quad \text{...(i)}$$

Similarly, $$t_{1/16}=\frac{2.303}{k}\log\frac{1}{1/16} \quad \text{...(ii)}$$

Dividing equation (ii) by (i)

$$\frac{t_{1/16}}{10}=\frac{\log 16}{\log 4} \Rightarrow t_{1/16}=10\times\frac{1.204}{0.6021}=20 \text{ minutes}$$

15. For first order reaction, $t=\dfrac{2.303}{k}\log\dfrac{[R_0]}{[R_t]}$

For 99% completion of reaction

$t = t_{0.99}$, $[R]_0 = 1$, $[R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$$t_{0.99}=\frac{2.303}{k}\log\frac{1}{10^{-2}}=\frac{2.303}{k}\log 10^2=\frac{2.303}{k}\times 2 \quad \text{...(i)}$$

For 90% completion of reaction

$t = t_{0.90}$, $[R]_0 = 1$, $[R]_t = (1–0.9) = 0.1 = 10^{-1}$

$$t_{0.90}=\frac{2.303}{k}\log\frac{1}{10^{-1}}=\frac{2.303}{k}\log 10=\frac{2.303}{k} \quad \text{...(ii)}$$

Comparing equations (i) and (ii),

$$t_{0.99} = 2 \times t_{0.90}$$

16. Change in concentration *i.e.*, either (decrease in concentration of reactant or increase in concentration of product) per unit time is called rate of reaction.

$$\text{Rate of reaction } = \frac{C_2-C_1}{t_2-t_1}=\frac{\Delta C}{\Delta t}$$

The ratio of change of concentration of reactants to the time consumed in that change is called average rate of reaction.

$$r_{av}=\frac{\Delta x}{\Delta t}=-\frac{C_2-C_1}{t_2-t_1}$$

The rate of reaction at a particular instant (time) is called instantaneous rate of reaction.

$$r_{ins}=\frac{dx}{dt}$$

d_x = small change in concentration

d_t = small time interval

17. (i) From the rate law equation, order of reaction w.r.t. B is 2. Hence, if concentration of B is doubled, rate will become four times.

(ii) If A is present in large excess, rate of reaction will be independent of concentration of A and hence, order of reaction will be 2.

18. For a first order reaction, $t=\dfrac{2.303}{k}\log\dfrac{[R]_0}{[R]}$

Given $k = 2.4 \times 10^{-3}\ s^{-1}$

$$[R]=\frac{[R]_0}{4}, t = ?$$

Substituting these values in the equation, we get

$$t=\frac{2.303}{2.4\times10^{-3}\ s^{-1}}\log\frac{[R]_0}{[R]}$$

$$t=\frac{2.303}{2.4\times10^{-3}s^{-1}}\log 4=\frac{2.303}{2.4\times10^{-3}}\times 0.6021\ s$$

t = 577.7 s = 578 s

19. (i) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

However, two molecules of ammonia react to give products thus, the molecularity is two.

(ii) For a zero order reaction, unit of rate constant is mol $L^{-1}\ s^{-1}$.

20. Given, $\dfrac{d[NO_2]}{dt}=2.8\times10^{-3}\,M\,s^{-1}$

According to rate law expression,

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt}=\frac{1}{4}\frac{d[NO_2]}{dt}=\frac{d[O_2]}{dt}$$

$$\therefore \quad -\frac{1}{2}\frac{d[N_2O_5]}{dt}=\frac{1}{4}\times 2.8\times 10^{-3}$$

$$\frac{-d[N_2O_5]}{dt}=\frac{1}{2}\times 2.8\times 10^{-3}=1.4\times 10^{-3}\,\mathrm{M\,s^{-1}}$$

21. Order of a reaction : It is the sum of the power of reactant in the rate law expression.

(i) L^{-1} mol s^{-1} – Zero order reaction

(ii) s^{-1} – First order reaction

22. (i) The reaction is of 1st order.

(ii) For first order reaction

$\ln[R] = -kt + \ln\,[R]_0$

comparing eqn. $y = m \times x + c$

we get a straight line with slope = $-k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

$$\frac{\mathrm{mol\,L^{-1}}}{\mathrm{s}}\times\frac{1}{(\mathrm{mol\,L^{-1}})^1}=\mathrm{s^{-1}}$$

23. For an elementary reaction, order should be equal to molecularity and further molecularity should be integral. For the given reaction, order of reaction = 1 + 1/2 = 3/2. Since molecularity cannot be fractional, therefore, for the given reaction, order is not equal to molecularity. Hence given reaction cannot be an elementary reaction.

24. (i) Differential rate equation of reaction is

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

(ii) When conc. of B is tripled, it means conc. of B becomes $[3 \times B]$

∴ New rate of reaction, $\dfrac{dx'}{dt}=k[A][3B]^2$

$$= 9k[A][B]^2 = 9\left(\frac{dx}{dt}\right)$$

i.e., the rate of reaction will become 9 times.

(iii) When conc. of A is doubled and that of B is also doubled, then conc. of A becomes $[2A]$ and that of B becomes $[2B]$.

∴ Now rate of reaction, $\dfrac{dx'}{dt}=k[2A][2B]^2 = 8k\,[A][B]^2$

i.e., the rate of reaction will become 8 times.

(iv) Molecularity of a reaction is the number of reacting particles which collide simultaneously to bring about the chemical change. It is a theoretical concept.

25. (i) Average rate of reaction between the time interval 30 to 60 seconds is

$$r_{av} = \frac{-[0.17-0.31]}{60-30}=\frac{0.14}{30}$$

$= 4.67 \times 10^{-3}\ \mathrm{s^{-1}}$ [Taking only difference]

(ii) $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]}$

At t = 30 s,

$$k=\frac{2.303}{30}\log\frac{0.55}{0.31}=\frac{2.303}{30}\times 0.249=1.91\times 10^{-2}\mathrm{s^{-1}}$$

At t = 60 s,

$$k=\frac{2.303}{60}\log\frac{0.55}{0.17}=\frac{2.303}{60}\times 0.5099=1.96\times 10^{-2}\mathrm{s^{-1}}$$

At t = 90 s

$$k=\frac{2.303}{90}\log\frac{0.55}{0.085}$$

$$k=\frac{2.303}{90}\times 0.8109=2.07\times 10^{-2}\mathrm{s^{-1}}$$

∴ Average value of k

$$=\frac{1.91\times 10^{-2}+1.96\times 10^{-2}+2.07\times 10^{-2}}{3}=1.98\times 10^{-2}\mathrm{s^{-1}}$$

26. The given rate law equation can be written as

$$-\frac{d[NH_3]}{dt}=\frac{k_1}{1/[NH_3]+k_2}$$

(i) If $[NH_3]$ is very high, $1/[NH_3]$ becomes negligible

$$\therefore \quad -\frac{d[NH_3]}{dt}=\frac{k_1}{k_2}=k$$

i.e., rate becomes independent of concentration. Hence, it is of zero order.

(ii) If $[NH_3]$ is is very small, $1/[NH_3]$ will be very large ($>>k_2$), so that k_2 can be neglected in comparison to $1/[NH_3]$. Hence $-\dfrac{d[NH_3]}{dt}=\dfrac{k_1}{1/[NH_3]}=k_1[NH_3]$

Thus, reaction is of 1st order.

27. The given data is

$$0.5\mathrm{mol L^{-1}}\xrightarrow{5\mathrm{min}}0.25\mathrm{mol L^{-1}}\xrightarrow{5\ \mathrm{min}}0.125\mathrm{mol L^{-1}}$$

Half life period is independent of initial concentration of the reactant, hence reaction is of first order.

For first order reaction

$$k=\frac{0.693}{t_{1/2}}=\frac{0.693}{5\ \mathrm{min}}=0.138\ \mathrm{min^{-1}}$$

28. (a) The formula of rate constant for first order reaction is

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

$$k_1 = \frac{2.303}{300\text{ s}} \log \frac{(1.6 \times 10^{-2})\text{ mol L}^{-1}}{(0.8 \times 10^{-2})\text{ mol L}^{-1}} = 2.3 \times 10^{-3}\text{ s}^{-1}$$

Similarly, $k_2 = \frac{2.303}{600\text{ s}} \log \frac{(1.6 \times 10^{-2})\text{ mol L}^{-1}}{(0.4 \times 10^{-2})\text{ mol L}^{-1}}$

$= 2.3 \times 10^{-3}\text{ s}^{-1}$

Unit and magnitude of rate constant shows the given reaction is of first order.

(b) The formula for half-life for first order reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.3 \times 10^{-3}\text{ s}^{-1}} = 301.30\text{ s}$$

29. Given : $[R]_0 = 1$, $[R] = 0.80$, $t = 160$ min

$t_{1/2} = ?$

For first order reaction, $k = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]}$

or, $k = \frac{2.303}{160} \log_{10} \frac{1}{0.8}$ or, $k = \frac{2.303}{160\text{ min}} \times \log 1.25$

or, $k = \frac{2.303 \times 0.0969}{160\text{ min}} = 1.39 \times 10^{-3}\text{ min}^{-1}$

Again $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.39 \times 10^{-3}} = 498$ min

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

Given $k = 1.06 \times 10^{-3}\text{ min}^{-1}$, $\frac{[A]_0}{[A]} = \frac{100}{85}$

$$t = \frac{2.303}{1.06 \times 10^{-3}\text{ min}^{-1}} \log \frac{100}{85}$$

$$t = \frac{2303}{1.06}[2\log 10 - \log 85]\text{min}$$

$$t = \frac{2303}{1.06}[2 \times 1 - 1.9294] = \frac{2303 \times 0.0706}{1.06}$$

$t = 153.39$ min $= 153.4$ min.

(ii) Given $k = 1.06 \times 10^{-3}\text{ min}^{-1}$, $\frac{[A]_0}{[A]} = \frac{100}{15}$

$$t = \frac{2.303}{1.06 \times 10^{-3}\text{ min}^{-1}} \log \frac{100}{15} = \frac{2303}{1.06}[2\log 10 - \log 15]\text{min}$$

$$= \frac{2303}{1.06}[2 \times 1 - 1.1761] = \frac{2303 \times 0.8239}{1.06}\text{min} = 1790\text{ min}$$

31. At pH = 5, as half-life period is found to be independent of initial concentration of sucrose, this means with respect to sucrose, it is a reaction of first order, *i.e.*, Rate = k[Sucrose]. If n is the order with respect to H^+ ion, $t_{1/2} \propto [H^+]^{1-n}$,

i.e., $500 \propto (10^{-5})^{1-n}$ [pH = 5 means $[H^+] = 10^{-5}$ M] ...(i)

and $50 \propto (10^{-6})^{1-n}$ [pH = 6 means $[H^+] = 10^{-6}$M] ...(ii)

Dividing (i) by (ii), $10 = (10)^{1-n}$ *i.e.* $1 - n = 1$ or $n = 0$, *i.e.*, order with respect to H^+ ion = 0. Hence, overall rate law is Rate = k [Sucrose] $[H^+]^0$.

32. The given reaction is $2N_2O_5 \rightarrow 4NO_2 + O_2$

Unit of rate constant suggests that rate of reaction is first order.

Hence, rate of reaction = $k[N_2O_5]$

$= 3.1 \times 10^{-4}\text{ min}^{-1} \times 0.40$ M

$= 1.24 \times 10^{-4}\text{ M min}^{-1}$

Rate of reaction,

$$= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

$$\therefore \quad -\frac{d[N_2O_5]}{dt} = 1.24 \times 10^{-4}\text{ M min}^{-1} \times 2$$

$= 2.48 \times 10^{-4}\text{ M min}^{-1}$

Similarly $\frac{d[NO_2]}{dt} = 4 \times 1.24 \times 10^{-4}\text{ M min}^{-1}$

$= 4.96 \times 10^{-4}\text{ M min}^{-1}$

$$+\frac{d[O_2]}{dt} = 1.24 \times 10^{-4}\text{ M min}^{-1}$$

33. The given reaction is

$$\begin{array}{llll} & SO_2Cl_{2(g)} \longrightarrow & SO_{2(g)} + & Cl_{2(g)} \\ \text{At } t = 0 & 0.4\text{ atm} & 0 & 0 \\ \text{At time } t & (0.4 - x)\text{ atm} & x\text{ atm} & x\text{ atm} \end{array}$$

Total pressure at time t will be

$P_t = (0.4 - x) + x + x = 0.4 + x$

$x = (P_t - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x = 0.4 - (P_t - 0.4) = 0.8 - P_t$

At time $t = 100$ s, $P_t = 0.7$ atm

$\therefore \quad p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation

$$k = \frac{2.303}{t} \log \frac{p_{SO_2Cl_2(\text{initial})}}{p_{SO_2Cl_2(\text{after reaction})}}$$

$$= \frac{2.303}{100} \log\left(\frac{0.4}{0.1}\right) = 1.3 \times 10^{-2}\text{ s}^{-1}$$

34. Let rate of reaction $r = k[A]^a[B]^b$

From the data

$r_1 = 0.10\text{ M s}^{-1} = k(1.0\text{ M})^a (0.20\text{ M})^b$ ... (i)

$r_2 = 0.20\text{ M s}^{-1} = k(2.0\text{ M})^a (0.20\text{ M})^b$ ... (ii)

$r_3 = 0.80\text{ M s}^{-1} = k(2.0\text{ M})^a (0.40\text{ M})^b$ ... (iii)

Dividing eqn. (i) by (ii)

$$\frac{r_1}{r_2} = \frac{0.10\text{ Ms}^{-1}}{0.20\text{ Ms}^{-1}} = \frac{k(1.0\text{ M})^a (0.20\text{ M})^b}{k(2.0\text{M})^a (0.20\text{ M})^b}$$

or, $\frac{1}{2}=\left(\frac{1}{2}\right)^a$ or $a = 1$

Dividing eqn. (ii) by eqn. (iii)

$$\frac{r_2}{r_3}=\frac{0.20\ \text{Ms}^{-1}}{0.80\ \text{Ms}^{-1}}=\frac{k(2.0)^a\,(0.20)^b}{k(2.0)^a\,(0.40)^b}\ \text{or,}\ \frac{1}{4}=\left(\frac{1}{2}\right)^b\ \text{or, } b=2$$

Hence, order of reaction = 1 + 2 = 3

35. The given reaction is

$$\begin{array}{llll} & C_2H_5Cl_{(g)} \longrightarrow & C_2H_{4(g)} + & HCl_{(g)} \\ \text{At time } t = 0 & 0.30\ \text{atm} & 0 & 0 \\ \text{At time } t = 300\ \text{sec} & 0.30 - x & x & x \end{array}$$

Total pressure $= 0.30 - x + x + x = 0.50$

or $\quad 0.30 + x = 0.50$

$\therefore \quad x = 0.50 - 0.30 = 0.20$

$\therefore$ Initial pressure, $P_0 = 0.30$ atm

Pressure of C_2H_5Cl after 300 sec,

$P_t = 0.30 - 0.20 = 0.10$ atm

Using formula for first order reaction,

$$k=\frac{2.303}{t}\log\left(\frac{P_0}{P_t}\right)$$

$$k=\frac{2.303}{300}\log\left(\frac{0.30}{0.10}\right)$$

$$k=\frac{2.303}{300}\log 3=\frac{2.303\times 0.4771}{300} = 3.66\times 10^{-3}\ \text{sec}^{-1}$$

36. (i) Let rate of reaction $\frac{d[N_2O_5]}{dt}=k[N_2O_5]^n$

$\therefore \quad r_1 = 0.10\ \text{mol L}^{-1}\ \text{hr}^{-1} = k\times(0.34\ \text{mol L}^{-1})^n$

$\quad\ \ r_2 = 0.20\ \text{mol L}^{-1}\ \text{hr}^{-1} = k\times(0.68\ \text{mol L}^{-1})^n$

$\quad\ \ r_3 = 0.40\ \text{mol L}^{-1}\ \text{hr}^{-1} = k\times(1.36\ \text{mol L}^{-1})^n$

$$\frac{r_1}{r_2}=\frac{0.10\ \text{mol L}^{-1}\text{hr}^{-1}}{0.20\ \text{mol L}^{-1}\text{hr}^{-1}}=\frac{k(0.34\ \text{mol L}^{-1})^n}{k(0.68\ \text{molL}^{-1})^n}$$

or $\quad \frac{1}{2}=\left(\frac{1}{2}\right)^n \quad \therefore n = 1$

(ii) Rate $= k\cdot[N_2O_5]$

$\therefore \quad 0.10\ \text{mol L}^{-1}\ \text{hr}^{-1} = k \times 0.34\ \text{mol L}^{-1}$

or $\quad k=\frac{0.10\ \text{mol L}^{-1}\ \text{hr}^{-1}}{0.34\ \text{mol L}^{-1}}$ or $k = 2.9\times 10^{-1}\ \text{hr}^{-1}$

37. For a first order reaction

$$k=\frac{0.6932}{t_{1/2}}=\frac{0.6932}{30}=0.0231\text{min}^{-1}$$

Suppose the reaction is

$$\begin{array}{lcc} & A \longrightarrow & \text{Products} \\ t = 0 & a & 0 \\ t = 70\ \text{min} & (a - x) & x \end{array}$$

$\therefore$ Fraction of the reactant remains unreacted $=\frac{(a-x)}{a}$

Now, $k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$ or $0.0231=\frac{2.303}{70}\log\left(\frac{a}{a-x}\right)$

$$\log\left(\frac{a}{a-x}\right)=\frac{0.0231\times 70}{2.303}=0.7021$$

or $\quad \frac{a}{a-x}$ = antilog 0.7021 = 5.036

$\therefore \quad \frac{a-x}{a}=\frac{1}{5.036} = 0.1985 \approx 0.2$

38. (i) For a first order reaction,

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

When $t = 30$ s

$$k=\frac{2.303}{30}\log\left(\frac{0.60}{0.30}\right)=\frac{2.303}{30}\times 0.3010 = 0.0231\ \text{s}^{-1}$$

When $t = 60$ s

$$k=\frac{2.303}{60}\log\left(\frac{0.60}{0.15}\right)=\frac{2.303}{60}\times 0.602= 0.0231\ \text{s}^{-1}$$

As the value of k is constant at different time intervals, the reaction is first order w.r.t. ester when $[H_2O]$ is constant. Hence, it is pseudo first order reaction.

(ii) Average rate $=-\frac{C_2-C_1}{t_2-t_1}=\frac{-(0.15-0.30)}{60-30}$

$$=\frac{0.15}{30}=5\times 10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

39. The given reaction is

$$\begin{array}{lcccc} & A_{(g)} \rightarrow & B_{(g)}\ + & C_{(g)}\ + & D_{(g)} \\ \text{Initial pressure} & P_o & 0 & 0 & 0 \\ \text{After 20 min.} & P_o - x & x & x & x \end{array}$$

Total pressure $= P_o - x + x + x + x = P_o + 2x$

$$P_o+2x=P_o+P_o\times\frac{40}{100}\ ;\ \frac{2x}{1}=\frac{P_o}{2.5}\ \text{or } P_o = 5x$$

$\therefore \quad x=\frac{P_o}{5}$

Now, $\quad [R]_0 = P_o$

$$[R]=P_o-x=P_o-\frac{P_o}{5} = 0.8\ P_o$$

Using formula, $k=\frac{2.303}{t}\log_{10}\frac{[R]_0}{[R]}$

or, $\quad k=\frac{2.303}{20\ \text{min}}\log_{10}\frac{P_o}{0.8P_o}$

or, $\quad k=\frac{2.303}{20\ \text{min}}\log 1.25 \quad$ or, $\quad k=\frac{2.303\times 0.0969}{20\ \text{min}}$

$\quad k = 1.115\times 10^{-2}\ \text{min}^{-1}$

40. Suppose order with respect to A is m and with respect to B is n. Then the rate law will be

Rate = $k[A]^m[B]^n$

Substituting the value of experiments 1 to 4, we get

Expt. 1 : Rate = $6.0 \times 10^{-3} = k\,(0.1)^m\,(0.1)^n$ ...(i)

Expt. 2 : Rate = $7.2 \times 10^{-2} = k\,(0.3)^m\,(0.2)^n$ ...(ii)

Expt. 3 : Rate = $2.88 \times 10^{-1} = k\,(0.3)^m\,(0.4)^n$...(iii)

Expt. 4 : Rate = $2.4 \times 10^{-2} = k\,(0.4)^m\,(0.1)^n$...(iv)

Comparing equation (i) and equation (iv),

$$\therefore \quad \frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k(0.1)^m\,(0.1)^n}{k(0.4)^m\,(0.1)^n}$$

$$\text{or,} \quad \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m$$

$\therefore \quad m = 1$

Comparing equation (ii) and equation (iii)

$$\frac{(\text{Rate})_2}{(\text{Rate})_3} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k(0.3)^m\,(0.2)^n}{k(0.3)^m\,(0.4)^n}$$

$$\text{or,} \quad \left(\frac{1}{2}\right)^2 = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n \quad \therefore \; n = 2$$

$\therefore$ Rate law expression is : Rate = $k[A][B]^2$

The rate constant can be calculated from the given data of any experiment using expression :

$$k = \frac{\text{Rate}}{[A][B]^2}$$

From expt. 1, $k = \dfrac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$

$\therefore$ Rate constant $k = 6.0$ mol^{-2} L^2 min^{-1}

Unit of k, $\dfrac{dx}{dt} = k[A]^1[B]^2 = 6.0[0.5][0.2]^2$

$= 6 \times 5 \times 4 \times 10^{-3} = 1.2 \times 10^{-1}$ mol L^{-1} min^{-1}

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