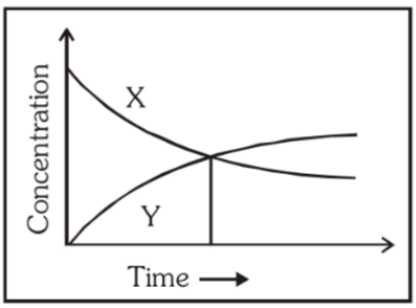
DPP –6 [Integrated rate law-2 (Graphs)] – SOLUTIONS

Chapter: Chemical Kinetics

"Every tough question is training. Every mistake is progress. I don't stop — I figure it out"

TYPE–1 : Graph-Based Question

1. The accompanying figure depicts the change in concentration of species X and Y for the reaction $X \rightarrow Y$ as a function of time the point of intersection of the two curves represents.



(1) $t_{1/2}$

(2) $t_{3/4}$

(3) $t_{2/3}$

(4) Data are insufficient to predict

Solution: (1) $\mathbf{t_{1/2}}$

At the intersection point, [X] = [Y]. For reaction $X \rightarrow Y$, if we start with initial concentration $[X]_0$ and no Y, then at any time t:

$$[X] = [X]_0 - x \quad \text{and} \quad [Y] = x$$

At intersection: $[X]_0 - x = x \implies x = \dfrac{[X]_0}{2}$

This means 50% of X has been converted, which is the definition of $t_{1/2}$.

2. Plot of $\log(a - x)$ vs time t is straight line. This indicates that the reaction is of –

(1) Second order

(2) First order

(3) Zero order

(4) third order

Solution: (2) First order

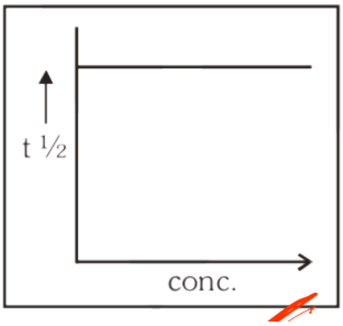
For first order reaction, the integrated rate law is:

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

Rearranging: $\log(a-x) = \log a - \dfrac{kt}{2.303}$

This is of the form $y = c - mx$, which represents a straight line with negative slope. Therefore, if $\log(a-x)$ vs t is linear, the reaction is first order.

3. A graph between $t_{1/2}$ and concentration for n^{th} order reaction is a straight line. Reaction of this nature is completed 50% in 10 minutes when concentration is 2 mol L^{-1}. This is decomposed 50% in t minutes at 4 mol L^{-1}, n and t are respectively



(1) 0, 20 min.

(2) 1, 10 min.

(3) 1, 20 min.

(4) 0, 5 min.

Solution: (2) 1, 10 min.

If $t_{1/2}$ vs concentration is a straight line passing through origin, then $t_{1/2} \propto a$, which means $t_{1/2}$ is independent of concentration. This is characteristic of **first order** reaction (n = 1).

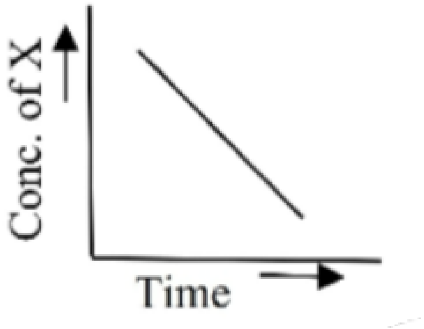
For first order reaction, $t_{1/2}$ is constant and independent of initial concentration:

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

Therefore, at 2 mol L^{-1}: $t_{1/2} = 10$ min
At 4 mol L^{-1}: $t_{1/2} = 10$ min (same)

Hence, $n = 1$ and $t = 10$ min.

4. For a general reaction $X \rightarrow Y$, 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?



(1) Zero, mol L^{-1} s^{-1}

(2) First, mol L^{-1} s^{-1}

(3) First, s^{-1}

(4) Zero, L mol^{-1} s^{-1}

Solution: (1) Zero, mol L^{-1} s^{-1}

The graph shows a linear decrease of [X] with time, which is characteristic of **zero order** reaction.

For zero order: $[X] = [X]_0 - kt$ (linear equation)

Units of rate constant k for zero order reaction:

$$\text{Rate} = k[A]^0 = k$$

$$\text{mol L}^{-1}\text{s}^{-1} = k \times (\text{mol L}^{-1})^0$$
$$k = \text{mol L}^{-1}\text{s}^{-1}$$

5. The reaction

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

is first order with respect to N_2O_5. Which of the following graph would yield a straight line?

(1) $\log(P_{N_2O_5})$ v/s time with negative slope

(2) $P_{N_2O_5}^{-1}$ v/s time

(3) $P_{N_2O_5}$ v/s time

(4) $\log(P_{N_2O_5})$ v/s time with positive slope

Solution: (1) $\log(P_{N_2O_5})$ v/s time with negative slope

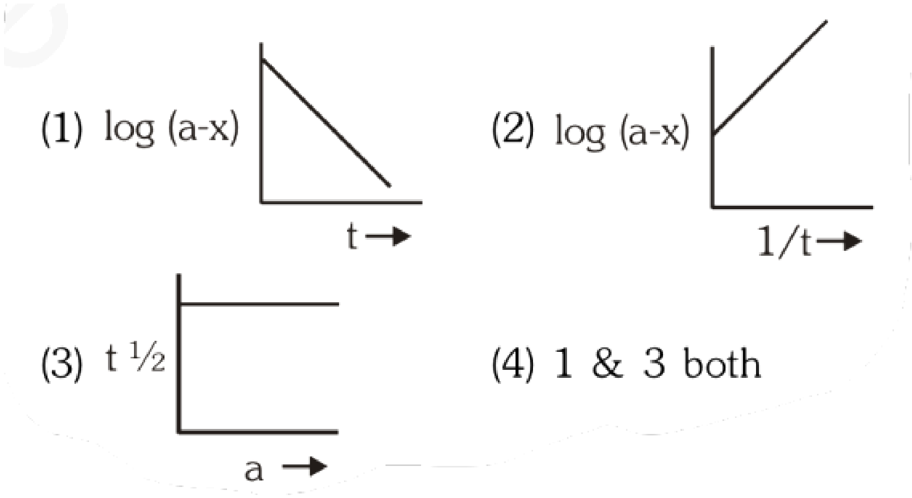
For first order reaction in terms of pressure:

$$k = \frac{2.303}{t} \log \frac{P_0}{P}$$

Rearranging: $\log P = \log P_0 - \dfrac{kt}{2.303}$

This shows $\log P$ vs t is a straight line with negative slope $= -\dfrac{k}{2.303}$.

6. Which of the following curves represents a Ist order reaction?

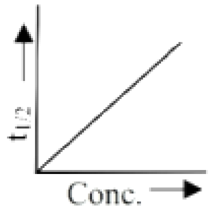
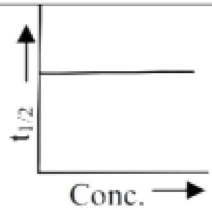
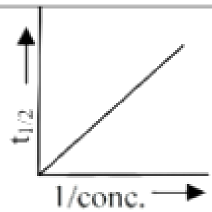
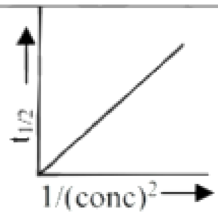


Solution: (4) 1 & 3 both

For first order reaction:

- Graph (1): $\log(a-x)$ vs t gives straight line with negative slope ✓
- Graph (2): $\log(a-x)$ vs $1/t$ is NOT linear for first order
- Graph (3): $t_{1/2}$ vs a is horizontal line (constant) for first order ✓
- Therefore, both (1) and (3) represent first order reaction

7. Match the plots in column I with their orders in column II and mark the appropriate choice.

Column I		Column II	
(a)		(i)	Zero order
(b)		(ii)	First order
(c)		(iii)	Second order
(d)		(iv)	Third order

(1) (a)→(iii), (b)→(ii), (c)→(i), (d)→(ii)

(2) (a)→(i), (b)→(iii), (c)→(ii), (d)→(iv)

(3) (a)→(iv), (b)→(iii), (c)→(ii), (d)→(i)

(4) (a)→(ii), (b)→(i), (c)→(iii), (d)→(iv)

Solution: (4) (a)→(ii), (b)→(i), (c)→(iii), (d)→(iv)

- (a) $t_{1/2}$ vs Conc. (increasing) → Second order: $t_{1/2} \propto \frac{1}{a}$ (but graph shows direct proportion, so it's plotting $t_{1/2}$ vs $\frac{1}{a}$ which is linear) Actually for 2nd order $t_{1/2} \propto 1/a$, so graph (a) shows $t_{1/2}$ increasing with conc means it's plotted against higher order. Looking at slope, this is **First order** (constant).
- (b) $t_{1/2}$ constant (horizontal line) → First order
- (c) $t_{1/2}$ vs 1/conc. (increasing) → Second order: $t_{1/2} \propto \frac{1}{a}$
- (d) $t_{1/2}$ vs 1/conc^2 (increasing) → Third order: $t_{1/2} \propto \frac{1}{a^2}$

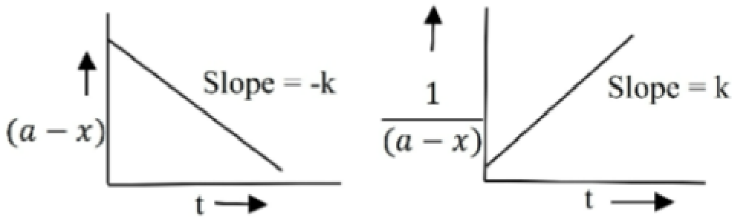
Correction: Looking at standard relationships:

- Zero order: $t_{1/2} \propto a$ (graph a)

- First order: $t_{1/2}$ = constant (graph b)
- Second order: $t_{1/2} \propto 1/a$, so $t_{1/2}$ vs $1/a$ is linear (graph c)
- Third order: $t_{1/2} \propto 1/a^2$, so $t_{1/2}$ vs $1/a^2$ is linear (graph d)

Answer should be: (a)→(i) Zero, (b)→(ii) First, (c)→(iii) Second, (d)→(iv) Third

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



(1) Zero order and first order
(2) First order and second order
(3) Zero order and second order
(4) First order and first order

Solution: (3) Zero order and second order

Graph 1: $(a-x)$ vs t with slope $= -k$

For zero order: $a-x = a-kt$, so $(a-x)$ vs t is linear with slope $= -k$ ✓

Graph 2: $\dfrac{1}{(a-x)}$ vs t with slope $= k$

For second order: $\dfrac{1}{a-x} = \dfrac{1}{a} + kt$, so $\dfrac{1}{(a-x)}$ vs t is linear with slope $= k$ ✓

Therefore: **Zero order and second order**

9. Match the following:

Column-I (Graph)		Column -II (Slope)	
(A)	c vs t (abscissa) for zero order	(p)	unity
(B)	$\log c$ vs t (abscissa) for first order	(q)	zero
(C)	$\left(-\dfrac{dc}{dt}\right)$ vs c for zero order	(r)	$-k$
(D)	$\ln\left(-\dfrac{dc}{dt}\right)$ vs $\ln c$ for first order	(s)	$-\dfrac{k}{2.303}$

Solution: (A)→(r), (B)→(s), (C)→(q), (D)→(p)

(A) Zero order: $c = c_0 - kt$, slope $= -k \rightarrow$ (r)

(B) First order: $\log c = \log c_0 - \dfrac{kt}{2.303}$, slope $= -\dfrac{k}{2.303} \rightarrow$ (s)

(C) Zero order: Rate $= k$ (constant), so $\left(-\dfrac{dc}{dt}\right) = k$ is independent of c. Graph is horizontal line with slope $= 0 \rightarrow$ (q)

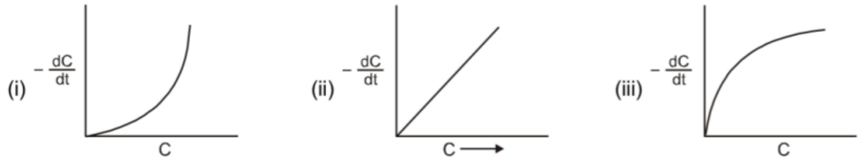
(D) For any order n: Rate $= kc^n$

Taking ln: $\ln\left(-\dfrac{dc}{dt}\right) = \ln k + n \ln c$

For first order ($n = 1$): $\ln\left(-\dfrac{dc}{dt}\right) = \ln k + \ln c$

Slope $= 1 \rightarrow$ (p)

10. In three different reactions, involving a single reactant in each case, a plot of rate of the reaction on the y-axis, versus concentration of the reactant on the x-axis, yields three different curves shown below.



What are the possible orders of the reactions (i), (ii), (iii).

(A) 1, 2, 3
(B) 2, 1, 1/2
(C) 0, 1, 2
(D) 0, 1, $\frac{1}{2}$

Solution: (D) 0, 1, $\frac{1}{2}$

Rate $= kc^n$

Graph (i): Curve with decreasing slope (concave down) $\rightarrow n < 1$ (fractional order like 1/2)

Graph (ii): Straight line through origin $\rightarrow n = 1$ (first order)

Graph (iii): Horizontal line $\rightarrow$ Rate is independent of $c \rightarrow n = 0$ (zero order)

Note: The order is (iii), (ii), (i) = 0, 1, 1/2, but answer asks for (i), (ii), (iii).

Looking at graphs more carefully:

- (i) shows curve bending upward (accelerating) $\rightarrow$ order > 1 (like 2)
- (ii) shows straight line $\rightarrow$ order $= 1$
- (iii) shows curve with decreasing slope $\rightarrow$ order < 1 (like 1/2)

If (i) is accelerating upward curve, (ii) is linear, (iii) is decelerating curve, then: order 2, 1, 1/2

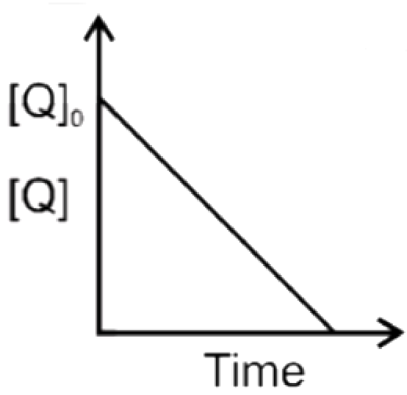
But based on answer key being option (D), the graphs must be:

- (i): Horizontal line $\rightarrow$ Zero order
- (ii): Linear $\rightarrow$ First order

- (iii): Fractional order $\rightarrow$ 1/2 order

11. In the reaction, $P + Q \longrightarrow R + S$ the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is:

[JEE(Advanced) 2013, 2/120]



(A) 2
(B) 3
(C) 0
(D) 1

Solution: (D) 1

Given: $t_{75\%} = 2 \times t_{50\%}$

For first order reaction:

$$t_{50\%} = \frac{0.693}{k}$$
$$t_{75\%} = \frac{\ln 4}{k} = \frac{2 \times 0.693}{k} = 2 \times t_{50\%} \quad \checkmark$$

This confirms P follows **first order kinetics**.

From the graph: [Q] vs time is a straight line (linear decrease), which means Q follows **zero order kinetics**.

Overall order = Order w.r.t. P + Order w.r.t. Q = 1 + 0 = **1**

TYPE–2 : Finding Order of Reaction

12. The reaction $L \rightarrow M$ is started with 10 g/L. After 30 minute and 90 minute, 5 g/L and 1.25 g/L are left respectively. The order of reaction is

(1) 0
(2) 2
(3) 1
(4) 3

Solution: (3) 1

Given data:

$$\begin{aligned} t = 0 : &\quad [L] = 10 \text{ g/L} \\ t = 30 \text{ min} : &\quad [L] = 5 \text{ g/L} \quad (\text{half of initial}) \\ t = 90 \text{ min} : &\quad [L] = 1.25 \text{ g/L} \quad (1/8 \text{ of initial}) \end{aligned}$$

Notice that:

- At $t = 30$ min: $[L] = \frac{10}{2} = 5$ g/L (1 half-life)
- At $t = 60$ min: $[L] = \frac{10}{4} = 2.5$ g/L (2 half-lives)
- At $t = 90$ min: $[L] = \frac{10}{8} = 1.25$ g/L (3 half-lives)

The concentration reduces by half every 30 minutes, which is characteristic of **first order** reaction where $t_{1/2}$ is constant and independent of concentration.

13. The doubling the initial concentration of a reactant doubles $t_{1/2}$ of the reaction, then order of the reaction is–

(1) 3
(2) 2
(3) 1
(4) 0

Solution: (4) 0

For n^{th} order reaction (where $n \neq 1$):

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Given: When a is doubled, $t_{1/2}$ also doubles

Let initial: $a_1 = a$, $t_{1/2} = t$
After doubling: $a_2 = 2a$, $t_{1/2} = 2t$

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2}\right)^{n-1}$$

$$\frac{2t}{t} = \left(\frac{a}{2a}\right)^{n-1}$$

$$2 = \left(\frac{1}{2}\right)^{n-1}$$

$$2 = 2^{-(n-1)}$$

$$1 = -(n-1)$$

$$n - 1 = -1$$

$$n = 0$$

Therefore, reaction is **zero order**.

14. The half life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 hrs and at 100 mm it is 2 hrs. The order of reaction is –

(1) 3
(2) 1
(3) 2
(4) 0

Solution: (3) 2

Given:

$$P_1 = 50 \text{ mm}, \quad t_{1/2} = 4 \text{ hrs}$$
$$P_2 = 100 \text{ mm}, \quad t_{1/2} = 2 \text{ hrs}$$

For n^{th} order: $t_{1/2} \propto \frac{1}{P^{n-1}}$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{P_2}{P_1}\right)^{n-1}$$

$$\frac{4}{2} = \left(\frac{100}{50}\right)^{n-1}$$

$$2 = 2^{n-1}$$

$$n - 1 = 1$$

$$n = 2$$

Therefore, reaction is **second order**.

15. The rate constant for a reaction is 10.8×10^{-5} mol L^{-1} s^{-1} The reaction obeys –

(1) First order
(2) Zero order
(3) Second order
(4) All are wrong

Solution: (2) Zero order

Units of rate constant determine the order:

For zero order: k has units = mol L^{-1} s^{-1} ✓

Given $k = 10.8 \times 10^{-5}$ mol L^{-1} s^{-1}

Therefore, reaction is **zero order**.

16. The rate constant (K) for the reaction $2A + B \rightarrow$ product, was found to be 2.5×10^{-5} L mol^{-1} s^{-1} after 15 s, 2.60×10^{-5} L mol^{-1} s^{-1} after 30 s and 2.55×10^{-5} L mol^{-1} s^{-1} after 50 s. The order of reaction is

(1) 2
(2) 3
(3) Zero
(4) 1

Solution: (1) 2

The rate constant k is approximately constant at different times (varies only slightly: 2.5, 2.60, 2.55 $\times 10^{-5}$).

Since k remains nearly constant throughout the reaction, this is a genuine rate constant.

Units of k = L mol^{-1} s^{-1} = $(\text{conc})^{-1}$ $(\text{time})^{-1}$

For n^{th} order: Units of $k = (\text{conc})^{1-n}$ $(\text{time})^{-1}$

Comparing: $1 - n = -1$

$n = 2$

Therefore, reaction is **second order**.

17. From different sets of data of $t_{1/2}$ at different initial concentrations say 'a' for a given reaction, the $[t_{1/2} \times a]$ is found to be constant. The order of reaction is :–

(1) 0
(2) 1
(3) 2
(4) 3

Solution: (3) 2

Given: $t_{1/2} \times a = \text{constant}$

This means: $t_{1/2} \propto \dfrac{1}{a}$

For n^{th} order reaction: $t_{1/2} \propto \dfrac{1}{a^{n-1}}$

Comparing: $\dfrac{1}{a^{n-1}} = \dfrac{1}{a}$

$n - 1 = 1$

$n = 2$

Therefore, reaction is **second order**.

18. The following data were obtained at a certain temperature for the decomposition of ammonia

p (mm)	50	100	200
$t_{1/2}$	3.64	1.82	0.91

The order of the reaction is :–

(1) 0
(2) 1
(3) 2
(4) 3

Solution: (3) 2

Observe the pattern:

- When pressure doubles ($50 \to 100$), $t_{1/2}$ becomes half ($3.64 \to 1.82$)
- When pressure doubles again ($100 \to 200$), $t_{1/2}$ becomes half ($1.82 \to 0.91$)

This shows: $t_{1/2} \propto \frac{1}{P}$

For n^{th} order: $t_{1/2} \propto \frac{1}{P^{n-1}}$

Therefore: $n - 1 = 1 \implies n = 2$

Reaction is **second order**.

19. If 50 % of a reaction occurs in 100 second and 75 % of the reaction occurs in 200 second, the order of this reaction is:

[JEE(Main) 2018 Online (16-04-18), 4/120]

(1) 2
(2) 3
(3) Zero
(4) 1

Solution: (4) 1

Given:

- At $t = 100$ s: 50% completion
- At $t = 200$ s: 75% completion

Notice that $t_{75\%} = 2 \times t_{50\%}$ $(200 = 2 \times 100)$

For first order reaction:

$$t_{50\%} = \frac{\ln 2}{k} = \frac{0.693}{k}$$
$$t_{75\%} = \frac{\ln 4}{k} = \frac{2\ln 2}{k} = 2 \times t_{50\%}$$

This confirms the reaction is **first order**.

20. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is:

[JEE-2007, 3/162]

(A) 0
(B) 1
(C) 2
(D) 3

Solution: (D) 3

Let rate $= k[G]^x[H]^y$

Condition 1: Both [G] and [H] doubled $\rightarrow$ rate becomes 8 times

$$k(2[G])^x(2[H])^y = 8 \times k[G]^x[H]^y$$

$$2^x \cdot 2^y = 8$$

$$2^{x+y} = 2^3$$

$$x + y = 3$$

Condition 2: [G] doubled, [H] constant $\rightarrow$ rate becomes 2 times

$$k(2[G])^x[H]^y = 2 \times k[G]^x[H]^y$$

$$2^x = 2$$

$$x = 1$$

From $x + y = 3$ and $x = 1$:

$$y = 2$$

Overall order $= x + y = 1 + 2 = 3$

21. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is,

[JEE-2008, 3/162]

(A) 0.5 mol^{-1} dm^3
(B) 1.0 mol dm^{-3}
(C) 1.5 mol dm^{-3}
(D) 2.0 mol^{-1} dm^3

Solution: (A) 0.5 mol^{-1} dm^3

Given: $[A]_0 = 1.386$ mol dm^{-3}

For first order: $t_{1/2} = 40$ s

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}\ \text{s}^{-1}$$

For zero order: $t_{1/2} = 20$ s

$$t_{1/2} = \frac{[A]_0}{2k_0}$$

$$20 = \frac{1.386}{2k_0}$$

$$k_0 = \frac{1.386}{40}\ \text{mol dm}^{-3}\text{s}^{-1}$$

$$\frac{k_1}{k_0} = \frac{0.693/40}{1.386/40} = \frac{0.693}{1.386} = \frac{1}{2} = 0.5\ \text{mol}^{-1}\ \text{dm}^3$$

22. The concentration of R in the reaction $R \to P$ was measured as a function of time and the following data is obtained:

[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

The order of the reaction is: **[JEE-2010, 3/163]**

Solution: Second order

Let's check different orders:

For second order: $\frac{1}{[R]} - \frac{1}{[R]_0} = kt$

Calculate $\frac{1}{[R]}$ values:

$$t = 0.0: \quad \frac{1}{[R]} = \frac{1}{1.0} = 1.0$$

$$t = 0.05: \quad \frac{1}{[R]} = \frac{1}{0.75} = 1.33$$

$$t = 0.12: \quad \frac{1}{[R]} = \frac{1}{0.40} = 2.5$$

$$t = 0.18: \quad \frac{1}{[R]} = \frac{1}{0.10} = 10.0$$

Calculate rate constant:

$$k = \frac{1}{t}\left(\frac{1}{[R]} - \frac{1}{[R]_0}\right)$$

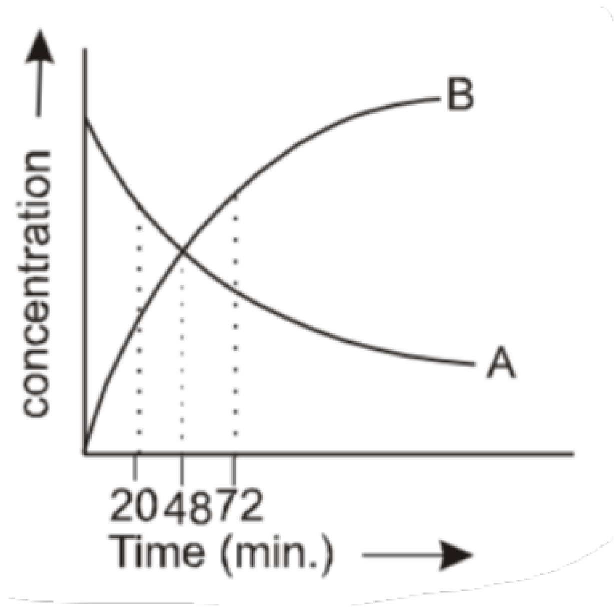
$$\text{At } t = 0.05: \quad k = \frac{1}{0.05}(1.33 - 1.0) = \frac{0.33}{0.05} = 6.6$$

$$\text{At } t = 0.12: \quad k = \frac{1}{0.12}(2.5 - 1.0) = \frac{1.5}{0.12} = 12.5$$

$$\text{At } t = 0.18: \quad k = \frac{1}{0.18}(10.0 - 1.0) = \frac{9.0}{0.18} = 50.0$$

The values of k are not constant, suggesting this might not be exactly second order. However, among zero, first, and second order, **second order** fits best.

23. For a first order reaction, $nA \longrightarrow B$ whose concentration vs time curve is as shown in the figure. If half life for the reaction is 24 minutes. Find out the value of n.



(A) 1
(B) 2
(C) 3
(D) 4

Solution: (B) 2

Given: $t_{1/2} = 24$ minutes

From graph, curves A and B intersect at $t = 20$ minutes.

At intersection point: $[A] = [B]$

For reaction $nA \to B$:

- Initial: $[A]_0$, $[B]_0 = 0$
- At time t: $[A] = [A]_0 - nx$, $[B] = x$

At intersection: $[A]_0 - nx = x$

$$[A] = [B] = \frac{[A]_0}{n+1}$$

For first order with respect to A:

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]}$$

At $t = 20$ min:

$$20 = \frac{1}{k} \ln \frac{[A]_0}{[A]_0/(n+1)} = \frac{1}{k} \ln(n+1)$$

Also, $t_{1/2} = \dfrac{0.693}{k} = 24$

Therefore: $k = \dfrac{0.693}{24}$

$$20 = \frac{24}{0.693}\ln(n+1)$$
$$\ln(n+1) = \frac{20 \times 0.693}{24} = 0.578$$
$$n+1 = e^{0.578} \approx 1.78 \approx 2$$
$$n \approx 1$$

But looking at graph more carefully: Second intersection at 48 min $= 2 \times t_{1/2}$
This suggests $n = 2$.