

EXERCISE # O-II

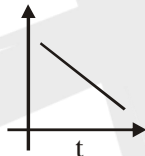
1. For a second order reaction plots are made for $\frac{1}{[A]}$ vs time for the reaction, $2A \longrightarrow \text{Product}$.

Pick up the correct sentences. [K = Rate constant of A]

- (A) the graph will show straight line with slope K
 (B) the graph will show straight line with intercept $[A]_0$
 (C) the graph will show straight line with slope $[A]_0$
 (D) the graph will show straight line with intercept $\frac{1}{[A]_0}$

2. For the reaction $A \rightarrow B$, the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of [A] is $[A]_0$, then

- (A) The integrated rate expression is $k = \frac{2}{t} (A_0^{1/2} - A^{1/2})$

- (B) The graph of \sqrt{A} vs t will be
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- (C) The half-life period $t_{1/2} = \frac{K}{2[A]_0^{1/2}}$

- (D) The time taken for 75% completion of reaction $t_{3/4} = \frac{\sqrt{[A]_0}}{k}$

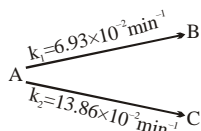
3. For the reaction $2A + B \longrightarrow C$ with the rate law $\frac{d[C]}{dt} = k[A]^1[B]^{-1}$ and started with A and B in stoichiometric proportion. Which is/are true?

- (A) unit of k is Ms^{-1}
 (B) [A], [B] and [C] all will be linear functions of time
 (C) $[C] = 2kt$
 (D) $[C] = kt$

4. Decomposition of $3 A(g) \longrightarrow 2 B(g) + 2C(g)$ follows first order kinetics. Initially only A is present in the container. Pressure developed after 20 min. and infinite time are 3.5 and 4 atm respectively. Which of the following is true.

(A) $t_{50\%} = 20$ min (B) $t_{75\%} = 40$ min (C) $t_{99\%} = 64/3$ min (D) $t_{87.5\%} = 60$ min

5. Consider the reaction,



A, B and C all are optically active compound. If optical rotation per unit concentration of A, B and C are 60° , -72° , 42° and initial concentration of A is 2 M then select write statement(s).

- (A) Solution will be optically active and dextro after very long time
 (B) Solution will be optically active and levo after very long time
 (C) Half life of reaction is 15 min
 (D) After 75% conversion of A into B and C angle of rotation of solution will be 36° .

6. For the reaction $\text{CH}_4 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr}$ the experimental data give the following rate equation:

$$\frac{d}{dt} [\text{CH}_3\text{Br}] = \frac{k_1 [\text{CH}_4] [\text{Br}_2]}{1 + k_2 [\text{HBr}] / [\text{Br}_2]}$$

Which of the following is/are true regarding this ?

- (A) The reaction is a single step reaction
 (B) The reaction is 2nd order in the initial stages $\{[\text{HBr}] \approx 0\}$
 (C) The reaction is 2nd order in the final stages $\{[\text{Br}_2] \approx 0\}$
 (D) The molecularity of the reaction is two

7. Which of the following is/are correct statement?

- (A) Stoichiometry of a reaction tells about the order of the elementary reactions.
 (B) For a zero order reaction, rate and the rate constant are identical.
 (C) A zero order reaction is controlled by factors other than concentration of reactants.
 (D) A zero order reaction is always elementary reaction.

8. Select incorrect statement(s):

- (A) Unit of pre-exponential factor (A) for second order reaction is $\text{mol L}^{-1} \text{s}^{-1}$.
 (B) A zero order reaction must be a complex reaction.
 (C) Molecularity is defined only for RDS in a complex reaction.

- (D) Rate constant (k) remain unaffected on changing temperature.
9. Which of the following statement is/are correct?
- (A) A second order reaction must be a bimolecular elementary reaction
(B) A bimolecular elementary reaction must be a second order reaction
(C) Order of reaction can't be predicted by stoichiometry of reaction.
(D) First order reaction may be complex or elementary reaction
10. Which of the following statements about the Arrhenius equation are correct ?
- (A) The pre-exponential factor become equal to the rate constant of the reaction at temperature T
(B) When the activation energy of the reaction zero, the rate becomes independent of temperature.
(C) The term $e^{-E_a/RT}$ represents the fractions of the molecules having energy in excess of the threshold value.
(D) On raising temperature, rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.
11. Consider a reaction $A(g) \longrightarrow 3B(g) + 2C(g)$ with rate constant $1.386 \times 10^{-2} \text{ min}^{-1}$. Starting with 2 moles of A in 12.5 litre vessel initially, if reaction is allowed to takes place at constant pressure & at 298K then find the concentration of B after 100 min.
- (A) 0.04 M (B) 0.36 M (C) 0.09 M (D) None of these

ASSERTION & REASONING TYPE QUESTIONS

12. **Statement-1** : The time of completion of reactions of type $A \rightarrow \text{product}$ (order < 1) may be determined.
- Statement-2** : Reactions with order ≥ 1 are either too slow or too fast and hence the time of completion can not be determined.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

13. **Statement-1** : In a reversible endothermic reaction, E_{act} of forward reaction is higher than that of backward reaction

Statement-2 : The threshold energy of forward reaction is more than that of backward reaction

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

14. **Statement-1** : A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly

Statement-2 : The catalyst forms an activated complex of lower potential energy, with the reactants by which more number of molecules are able to cross the barrier per unit of time.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

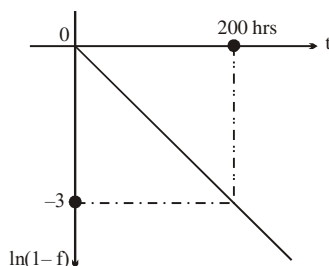
(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

COMPREHENSION

Paragraph for Question Nos. 15 & 16

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal $(1 - f)$ surface thickness relative to maximum thickness (T) of oxidised surface, when metal surface is exposed to air for considerable period of time



Rate law : $= k(1 - f)$, where $f = x/T$, x = thickness of oxide film at time 't' & T = thickness of oxide film at $t = \infty$

A graph of $\ln(1 - f)$ vs t is shown in the adjacent figure.

15. The time taken for thickness to grow 50% of 'T' is
 (A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs
16. The exponential variation of 'f' with t(hrs) is given by
 (A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$ (C) $e^{-3t/200}$ (D) $e^{3t/200}$

Paragraph for Question No. 17 & 18

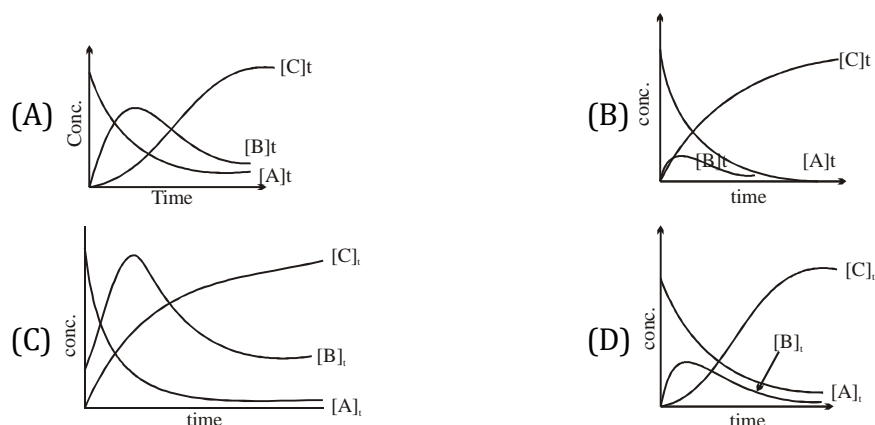
For the given sequential reaction



the concentration of A, B & C at any time 't' is given by

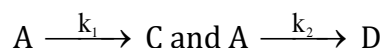
$$[A] = [A]_0 e^{-k_1 t} \quad [B]_t = \frac{k_1 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \quad [C]_t = [A]_0 - ([A]_t + [B]_t)$$

17. The time at which concentration of B is maximum is
 (A) $\frac{k_1}{k_2 - k_1}$ (B) $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$ (C) $\frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$ (D) $\frac{k_2}{k_2 - k_1}$
18. Select the correct option if $k_1 = 1000 \text{ s}^{-1}$ and $k_2 = 20 \text{ s}^{-1}$.



Paragraph for Question No. 19 to 20

Frequently a species can react in different ways to give a variety of products. For example, toluene can be nitrated at the ortho, meta, or para positions, We shall consider the simplest case, that of two competing irreversible first-order reactions :



where the stoichiometric coefficients are taken as unity for simplicity. The rate law is

$$\left(\frac{d[A]}{dt} \right) = -k_1[A] - k_2[A] = -(k_1 + k_2) [A] \quad \Rightarrow \quad [A] = [A]_0 e^{-(k_1+k_2)t}$$

For C, we have $\left(\frac{d[C]}{dt} \right) = k_1[A] = k_1[A]_0 e^{-(k_1+k_2)t}$. Multiplication by dt and integration from time 0

(where $[C]_0 = 0$) to an arbitrary time t gives $[C] = \frac{k_1[A]_0}{k_1 + k_2} (1 - e^{-(k_1+k_2)t})$

Similarly, integration of gives $\left(\frac{d[D]}{dt} \right) [D] = \frac{k_2[A]_0}{k_1 + k_2} (1 - e^{-(k_1+k_2)t})$

The sum of the rate constants $k_1 + k_2$ appears in the exponentials for both [C] and [D].

At any time we also have $\frac{[C]}{[D]} = \frac{k_1}{k_2}$

19. $A \begin{cases} \xrightarrow{k_1} 2B \\ \xrightarrow{k_2} 3C \end{cases}$ starting initially with only A Which of the following is correct at time t

(A) $[A]_0 = [A]_t + [B]_t + [C]_t$ (B) $[A]_0 = [A]_t + 2[B]_t + 3[C]_t$

(C) $[A]_0 = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$ (D) $[A]_0 = \frac{2}{3} [A]_t + [B]_t + [C]_t$

20. $X \begin{cases} \xrightarrow{k_1} Y \\ \xrightarrow{k_2} Z \end{cases}$ starting with only 'X', ratio $\frac{[X]_t}{[Y]_t + [Z]_t}$

(A) Independent of time

(B) $\frac{1}{(e^{kt} - 1)}$

(C) Depends upon initial concentration of X

(D) $[A]_0 (e^{kt} - 1)$

21. At high temperature acetic acid decomposes into CO_2 & CH_4 and simultaneously into CH_2CO (ketene) and H_2O



What is the fraction of acetic acid reacting as per reaction (i) ?

- (A) $\frac{3}{4}$ (B) $\frac{3}{7}$ (C) $\frac{4}{7}$ (D) none of these

22. For A $\begin{matrix} \nearrow k_1 \rightarrow 3\text{B} \\ \searrow k_2 \rightarrow 4\text{C} \end{matrix}$ starting with pure A ratio of rate of production of B to C is :

- (A) Independent of time
(B) Independent of temperature
(C) Depends upon initial concentration of A
(D) Independent of mechanism of reaction

MATCH THE COLUMN

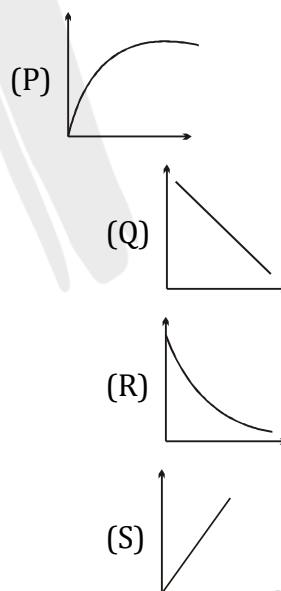
23. For the reaction of type $\text{A}(\text{g}) \longrightarrow 2\text{B}(\text{g})$

Column-I contains four entries and **column-II** contains four entries. Entry of column-I are to be matched with **ONLY ONE ENTRY** of column-II

Column I

- (A) $\frac{d[\text{B}]}{dt}$ vs $\frac{-d[\text{A}]}{dt}$ for first order
(B) $[\text{A}]$ vs t for first order
(C) $[\text{B}]$ vs t for first order
(D) $[\text{A}]$ vs t for zero order

Column II



24. Match the column :

Column-I	Column-II
(A) Inversion of cane sugar in excess water.	(P) Not 100% complete
(B) Saponification reaction with 1M NaOH	(Q) Psuedo-first order
(C) Decomposition of HI on gold	(R) Zero order
(D) Radioactive decay	(S) Conc. of reactant varies exponentially with time

25. Match the Column :

Column-I	Column-II
(Type of PLOT for reaction $A \rightarrow$ products)	
(A) Rate (y-axis) Vs $[A]_t$ (x-axis) for second order reaction	(P) Non-linear
(B) Half-life (y-axis) Vs initial concentration of A(x-axis) for second order reaction	(Q) Positive slope
(C) Rate (y-axis) Vs $\frac{1}{[A]_t}$ (x-axis) for zero order reaction	(R) Zero slope
(D) Log (Rate) (y-axis) vs time (x-axis) for first order reaction	(S) Linear

ANSWER KEY

EXERCISE # O-II

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|--|----------|-------------------------------|----------|-----------|
| 1. (AD) | 2. (ABD) | 3. (ABC) | 4. (ABD) | 5. (AD) |
| 6. (BC) | 7. (ABC) | 8. (ACD) | 9. (BCD) | 10. (ABC) |
| 11. (C) | 12. (C) | 13. (C) | 14. (A) | 15. (B) |
| 16. (A) | 17. (C) | 18. (C) | 19. (C) | 20. (B) |
| 21. (B) | 22. (A) | 23. A- S ; B- R ; C- P; D - Q | | |
| 24. $A \rightarrow P, Q, S$; $B \rightarrow P, Q, S$; $C \rightarrow R$; $D \rightarrow P'$ | | | | |
| 25. $A \rightarrow P, Q$; $B \rightarrow P$; $C \rightarrow R, S$; $D \rightarrow S$ | | | | |

