Chapter 4

Chemical Kinetics and Nuclear Chemistry

Solutions

SECTION - A

Objective Type Questions (One option is correct)

1. Consider the elementary reaction

   $aA + bB \rightarrow$ Product

   If only conc. of A is doubled, rate becomes four times. If conc. of B is made four times, rate becomes double. Select the correct statement w.r.t above reaction.

   (1) Overall order of reaction is two

   (2) Rate of disappearance of B is four times as that of A

   (3) Rate of disappearance of A is four times as that of B

   (4) Rate of reaction is half the rate of disappearance of B

Sol. Answer (3)

$R = K[A]^a [B]^b$

From given data, a = 2 and $b = \frac{1}{2}$

$\therefore R = \frac{-d[A]}{2dt} = \frac{-2d[B]}{dt}$

2. Consider the following equilibrium reaction:

$X \rightleftharpoons Y$

Rate of disappearance of reactant X at two different temperature is given as

$\frac{-d[X]}{dt} = 3\times10^{-1}[X] - 3\times10^{-2}[Y]$ at 27°C

$\frac{-d[X]}{dt} = 12\times10^{-1}[X] - 4\times10^{-2}[Y]$ at 127°C

Calculate the heat of reaction (assuming it to be constant in the given temperature range) when equilibrium is set up (approx)

(1) 32 kJ (2) 11 kJ (3) – 24 kJ (4) –48 kJ

Sol. Answer (2)

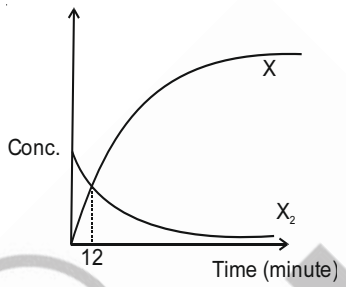
$$\left(K_{eq}\right)_{300\,K} = \frac{3\times10^{-1}}{3\times10^{-2}} = 10$$

$$\left(K_{eq}\right)_{400\,K} = \frac{12\times10^{-1}}{4\times10^{-2}} = 30$$

$$\therefore \Delta H = \frac{2.303\ R\ T_1\ T_2}{(T_2 - T_1)}\ \log\frac{30}{10}$$

3. Consider the following graph for a 1st order reaction:

$X_2(g) \rightarrow 2X(g)$



Select the correct statement (use ln2 = 0.7 and ln 3 = 1.1)

(1) Half life of reaction is 21 minute
(2) Rate constant of reaction is 0.048 minute^{-1}
(3) At 12 minute reaction is 66.7% completed
(4) Average life of reaction is 60 minute

Sol. Answer (1)

At t = 12 min $\underset{a-x}{X_2(g)} \longrightarrow \underset{2x}{2X(g)}$

$\because\ a - x = 2x \Rightarrow x = \frac{a}{3}$

$\therefore\ K \times 12 = \ln\frac{3}{2}$

$$t_{1/2} = \frac{\ln2\times12}{\ln3-\ln2} = 21 \text{ minutes}$$

$K = 0.033$ minutes^{-1}

Average life = $\frac{1}{K} = 30$ minutes

4. Consider the following reaction :

$X + 2Y \rightarrow$ Product

Experiment	[X]	[Y]	Initial rate
1	0.2	0.01	4×10^{-3}
2	0.1	0.01	2×10^{-3}
3	0.4	0.02	8×10^{-3}

From the above data the rate constant for the reaction is

(1) 4×10^{-2} mol lit^{-1} s^{-1}
(2) 2×10^{-2} s^{-1}
(3) 2×10^{-2} mol lit^{-1} s^{-1}
(4) 4×10^{-2} mol^{-1} lit s^{-1}

Sol. Answer (2)

From given data :

$R = K[X]^1\ [Y]^0$

$K = \dfrac{4\times10^{-3}}{0.2} = 2\times10^{-2}\ \text{sec}^{-1}$

5. For a reaction : $X + 2Y \rightarrow$ Products, if the rate of disappearance of Y is given expression:

$\dfrac{-dY}{dt} = (0.5\ \text{second}^{-1})\ [X]$

If initial concentration of X is $[X]_0$ then the concentration of X after 8 seconds is

(1) $\dfrac{[X]_0}{e^2}$ (2) $\dfrac{[X]_0}{e}$ (3) $[X]_0.e^2$ (4) $[X]_0\, e$

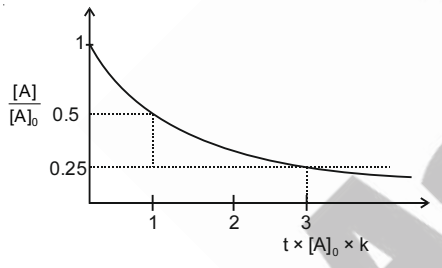
Sol. Answer (1)

$\text{Rate} = -\dfrac{1}{2}\dfrac{dY}{dt} = \dfrac{0.5}{2}[X] = -\dfrac{dX}{dt}$

$X = [X]_0\, e^{-kt}$

$X = [X]_0\, e^{\frac{0.5}{2}\times8} = \dfrac{[X]_0}{e^2}$

6. For reaction $A \xrightarrow{K}$ Products consider the graph



The order of reaction is

(1) Zero (2) First order (3) Second order (4) Third order

Sol. Answer (3)

For 2nd order reaction

$\dfrac{1}{A_t} = \dfrac{1}{A_0} + kt$

$\Rightarrow \dfrac{1}{A_t} = \dfrac{1+A_0kt}{A_0}$

$\Rightarrow \dfrac{A_0}{A_t} = 1+ktA_0$

$\Rightarrow \dfrac{1}{Y} = 1 + X$

$\Rightarrow (X + 1)\ Y = 1$

Hyperbolic graph

7. Which of the following type of emission occurs for $^{87}_{36}Kr$ changing to $^{87}_{37}Rb$ and how $\frac{n}{p}s$ ratio is affected ?

(1) Alpha emission – *n/p* increases
(2) Beta emission – *n/p* decreases
(3) Positron emission – *n/p* increases
(4) K-electron capture – *n/p* decreases

Sol. Answer (2)

8. Among the four radioactive disintegration series , $^{227}_{89}Ac$ belongs to

(1) Uranium series (2) Neptunium series (3) Thorium series (4) Actinium series

Sol. Answer (4)

9. Weight ratio of ^{206}Pb : ^{238}U in a pitchblende sample is 0.4 : 1. If all ^{206}Pb is supposed to be originated from ^{238}U, the age of the mineral (in year) is (Disintegration constant of ^{238}U is 1.5×10^{-10} per year) (log 1.462 = 0.165)

(1) 2.53×10^9 (2) 5×10^8 (3) 6×10^6 (4) 8×10^{10}

Sol. Answer (1)

$$^{238}U \rightarrow {}^{206}Pb$$

t = 0 N_0 0

t = t $N_0 - x$ x

$$\frac{x}{N_0 - x} = \frac{\frac{0.4}{206}}{\frac{1}{238}} = 0.462$$

Adding 1 both sides,

$$\Rightarrow \frac{N_0}{N_0 - x} = 1.462$$

$$t = \frac{2.303}{\lambda} \log 1.462$$

10. Consider the following radioactive decay

$$^{90}X \xrightarrow{\beta\text{-emission}} {}^{90}Y \xrightarrow{\beta\text{-emission}} Z$$

If half life of ^{90}Y is 73 hours and that of ^{90}X is 20 years, then the amount of ^{90}Y in equilibrium with 1 g of ^{90}X is

(1) 1 g (2) 0.5 g (3) 4.16×10^{-4} g (4) 2.08×10^{-4} g

Sol. Answer (3)

$$\frac{\text{Moles of } {}^{90}Y}{\text{Moles of } {}^{90}X} = \frac{(t_{1/2})_Y}{(t_{1/2})_X}$$

$$\Rightarrow \frac{w/90}{1/90} = \frac{73}{20 \times 365 \times 24}$$

$\Rightarrow w = 4.16 \times 10^{-4}$ g

11. Consider the following radioactive decay of ^{238}U

$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He^{2+}$

In a closed vessel of 11.2 ml 5.95 g of uranium is taken , then the total pressure at the end of 36 years at 0°C is ($t_{1/2}$ of $^{238}_{92}U$ is 12 years)

(1) 1 atm (2) 20 atm (3) 35 atm (4) 43.7 atm

Sol. Answer (4)

Moles of $^{4}_{2}He^{2+}$ at the end of 36 years = $\left(\frac{1}{2}\times\frac{1}{40}+\frac{1}{4}\times\frac{1}{40}+\frac{1}{8}\times\frac{1}{40}\right)$

$= \frac{1}{40}\times\frac{7}{8}$ moles

Pressure = $\frac{7}{8}\times\frac{1}{40}\times\frac{0.0821\times273\times1000}{11.2} = 43.7$

12. If M^{2+} is radioactive with α-emission, then the correct order of radioactivity of following substances is:

(I) 1 g MO (II) 1 g MSO_4 (III) 1g MCl_2 (IV) 1 g MS

(1) I > II > III > IV (2) IV > III > II > I (3) I > IV > III > II (4) I > IV > II > III

Sol. Answer (3)

$-\frac{dN}{dt} \propto$ Number M^{2+} ions

13. Consider the following statements:

(I) If $\left(\frac{K_{T+10}}{K_T}\right)$ is defined as the temperature coefficient, then its value decreases with temperature.

(II) Catalyst does not participate in reaction

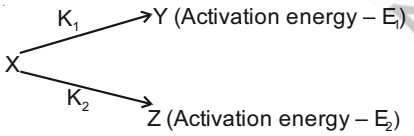
The correct statements is/are

(1) Only (I) (2) Only (II) (3) Both (I) and (II) (4) Neither (I) nor (II)

Sol. Answer (1)

Catalyst participates in reaction but does not get consumed in the reaction.

14. Consider the following parallel reaction:



Select the expression which correctly represents the activation energy corresponding to overall rate constant.

(1) $E_1 + E_2$ (2) $K_1E_1 + K_2E_2$ (3) $\frac{E_1}{K_1}+\frac{E_2}{K_2}$ (4) $\frac{K_1E_1+K_2E_2}{K_1+K_2}$

Sol. Answer (4)

$K = K_1 + K_2$

$\Rightarrow Ae^{-E/RT} = A_1\ e^{-E_1RT} + A_2\ e^{-E_2RT}$

Differentiating w.r.t. $\frac{1}{T}$

$$\Rightarrow \frac{E}{R}.K = \frac{E_1}{R}K_1 + \frac{E_2}{R}K_2$$

$$\Rightarrow E = \frac{E_1K_1 + E_2K}{K_1 + K_2}$$

15. Consider the following reactions:

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3;\ E_{act} = E_1$$

$$2SO_2 + O_2 \rightarrow 2SO_3\ ;\ E_{act} = E_2$$

The correct reaction between E_1 and E_2 is

(1) $E_1 = E_2$

(2) $E_1 = 2E_2$

(3) $E_1 = \frac{E_2}{2}$

(4) Cannot be predicted without actual value of E_1 and E_2

Sol. Answer (1)

Activation energy is an intensive property and it is independent of stoichiometric co-efficient of the reaction.

16. Consider the 1st order reaction in a closed vessel.

$X(S) \rightarrow Y(g) + 2Z(g)$

If total pressure in vessel after time '*t*' is P and after a very long time it is P_∞, then the correct expression for rate constant is

(1) $\frac{2.303}{t}\log\left(\frac{3P_\infty}{P_\infty - P}\right)$ (2) $\frac{2.303}{t}\log\left(\frac{3P_\infty}{P_\infty - 3P}\right)$

(3) $\frac{2.303}{t}\log\left(\frac{P_\infty}{P_\infty - P}\right)$ (4) $\frac{2.303}{t}\log\frac{P_\infty}{3(P_\infty - P)}$

Sol. Answer (3)

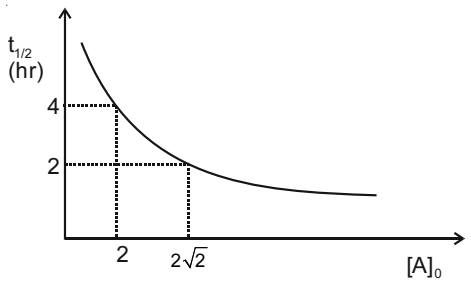
	$X(s) \longrightarrow$	$Y(g)$	$+ 2Z(g)$
$t = 0$	a		
$t = t$	$a - x$	x	$2x$
$t = \infty$	0	a	2a

$P \propto 3x$

$P_\infty \propto 3a$

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

17. For a reaction A → Product; the graph of half life versus initial concentration of reactant is given as



The order of reaction is

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

Sol. Answer (4)

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$$4 \propto \frac{1}{2^{n-1}}$$

$$2 \propto \frac{1}{(2\sqrt{2})^{n-1}}$$

$$\therefore \quad 2 = 2^{\frac{n-1}{2}}$$

$$\Rightarrow n = 3$$

18. Consider a hypothetical 1st order reaction:

P(aq.) → 2Q (aq) + R (aq)

'P' is optically active while Q and R are optically inactive and Q takes part in a titration reaction (fast) with H_2O_2. Progress of reaction can be examined either by measuring rotation of plane polarized light or by measuring volume of H_2O_2 consumed in reaction with Q. In an experiment optical rotation was equal to θ = 52° at t = 26 min and θ = 26° at t = 46 min from the start of reaction. If progress is to be monitored by measuring volume of H_2O_2 and if at t = 20 min from start, volume of H_2O_2 consumed is 24 mL then the volume of H_2O_2 consumed at t = 60 min from start is

(1) 72 mL (2) 42 mL (3) 48 mL (4) 36 mL

Sol. Answer (2)

θ = 52° at t = 26 minutes

θ = 26° at t = 46 minutes

$\therefore$ $t_{1/2}$ = 20 minutes

$\therefore$ At t = 60 minutes, volume of H_2O_2 consumed is

$$= 24 + \frac{24}{2} + \frac{24}{4}$$

= 24 + 12 + 6 = 42 mL

19. The correct statement among following is

(1) Gamma rays are more penetrating in nature than α-rays as they move with more velocity than α–rays

(2) α-rays are almost 10000 times more ionising than β(beta) rays

(3) Disintegration is spontaneous and its rate is affected by external factors like temperature and pressure

(4) Hydrolysis of ethyl acetate in alkine medium is second order reaction

Sol. Answer (4)

20. Select the correct statement about artificial radioactive disintegration series.

(1) Series starts with $_{90}Th^{232}$

(2) Last element of the series is $_{83}Bi^{209}$

(3) Total 6α-particles (per nuclei of starting element) are emitted during the disintegration

(4) Total 8 β-particles (per nuclei of starting element) are emitted during the disintegration

Sol. Answer (2)

21. Consider the following statements:

I – If a reaction has zero activation energy, its rate is independent of temperature

I – A high activation energy signifies that the rate constant depends strongly on temperature

III – For equilibrium $A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$, on increasing temperature, $\frac{dK_f}{dT} > \frac{dK_b}{dT}$ is observed, then the reaction must be endothermic in nature

Correct statements are

(1) Only I (2) Only I and II (3) Only II and III (4) I, II and III

Sol. Answer (4)

22. The activation energy of a 2nd order reaction is 100 kJ at 27°C. When the same reaction proceed with positive catalyst, the new activation energy is 71.13 kJ. The ratio of specific rate constant of catalyzed to uncatalyzed reaction is (approx)

(1) 10^5 (2) 10^3 (3) 10^7 (4) 10^8

Sol. Answer (1)

23. Select the incorrect statement.

(1) For 1st order reaction unit of rate constant is second^{-1}

(2) All radioactive decay follow 1st order kinetics

(3) Zero order reaction takes finite time to complete

(4) In 1st order reaction, in equal time equal amount of reactant reacts

Sol. Answer (4)

24. Consider the following statements SI, SII and SIII

SI. The number of collisions per unit volume per unit time is called as frequency factor

SII. Collision theory assumes molecules to be hard spheres

SIII. Steric factor deals with the orientation of molecules

The correct among these are

(1) SI and SII only (2) SII and SIII only (3) SI and SIII only (4) SI, SII and SIII

Sol. Answer (2)

Given definition is for collision frequency(Z) frequency factor is A.

25. The rates of radioactive decay of a sample are 3×10^8 dps and 3×10^7 dps after 20 minutes and 43.03 minutes respectively. The fraction of radioactive atoms remaining after the first minute is equal to (log 3 = 0.477)

(1) $\frac{1}{600}$ (2) 0.90 (3) 0.44 (4) 0.001

Sol. Answer (2)

Rate = λ N

$r_{20} = \lambda N_{20} = N_o \lambda e^{-20\lambda} = 3 \times 10^8$

$r_{43.03} = \lambda N_{43.03} = \lambda N_0 e^{-43.03\lambda} = 3 \times 10^7$

$\therefore \frac{e^{-20\lambda}}{e^{-43.03\lambda}} = 10$

$\Rightarrow e^{+23.03\lambda} = 10$

$\Rightarrow \lambda = 0.1 \text{ min}^{-1}$

$\therefore$ Fraction remaining after the first minute = $\frac{Nt}{N_0} = e^{-\lambda t}$

$= e^{-0.1 \times 1} = e^{-0.1}$

$\simeq 0.9$

SECTION - B

Objective Type Questions (More than one options are correct)

1. For the reaction A + B $\longrightarrow$ 2C + D. Which of the following statement is/are correct?

(1) Rate of disappearance of $B = \frac{1}{2}$ × rate of appearance of C

(2) Rate of disappearance of B = 2 × rate of appearance of C

(3) Rate of disappearance of A = rate of appearance of D

(4) Rate of disappearance of A = rate of disappearance of B

Sol. Answer (1, 3, 4)

We can relate rate for the reaction

A + B $\rightarrow$ 2 C + D as :

$$\frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t} = \frac{+\Delta[D]}{\Delta t}$$

We can conclude that (1), (3) & (4) are correct answer. (2) is not correct because

$$\frac{-\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$$

2. In the formation of sulphur trioxide by the contact process, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of reaction was measured as $\frac{-d(SO_2)}{dt} = 6.0 \times 10^{-4}$ mol $L^{-1}s^{-1}$. Select correct statements.

(1) The rate of reaction expressed in terms of SO_3 will be 6.0×10^{-4} mole $L^{-1}s^{-1}$

(2) The rate of reaction expressed in terms of O_2 will be 6.0×10^{-4} mole $L^{-1}s^{-1}$

(3) The rate of reaction expressed in terms of O_2 will be 3.0×10^{-4} mole $L^{-1}s^{-1}$

(4) The rate of reaction expressed in terms of O_2 will be 12×10^{-4} mole $L^{-1}s^{-1}$

Sol. Answer (3)

3. The rate law for the reaction, RCl + NaOH $\longrightarrow$ ROH + NaCl is given by Rate = K[RCl]. The rate of the reaction is

(1) Doubled by doubling the concentration of NaOH

(2) Halved by reducing the concentration of RCl by one half

(3) Increased by increasing the temperature of the reaction

(4) Unaffected by change in temperature

Sol. Answer (2, 3)

The rate law is given by

Rate = K [RCl]

For reaction, RCl + NaOH $\rightarrow$ ROH + NaCl .

The rate $\propto$ [RCl] hence when [RCl] reduces to half, rate also becomes half and is not affected by [NaOH].

The rate always increases with the increase in temperature.

4. Which of the following statements for order of a reaction are correct?

(1) Order can be determined experimentally

(2) Order of reaction is equal to sum of the power of concentration terms in differential rate law

(3) It is not affected by the stoichiometric coefficient of the reactants

(4) Order can be fractional

Sol. Answer (1, 2, 3, 4)

For any reaction we can write the rate law

$$\frac{dx}{dt} = K[A]^{\alpha}\,[B]^{\beta}$$

Order is purely an experimental quantity which cannot be determined by stoichiometry of reaction. It can be +ve, –ve, fractional or zero and order = $(\alpha + \beta)$.

5. In a hypothetical reaction,

$A_2 + B_2 \longrightarrow 2AB$

follows the mechanism as given below

$A_2 \rightleftharpoons A + A$(fast reaction)

$A + B_2 \longrightarrow AB + B$ (slow reaction)

$A + B \longrightarrow AB$ (fast reaction)

Select the correct statement.

(1) $R = k[A]^2\,[B_2]$

(2) Order of reaction is $\frac{3}{2}$

(3) Molecularity is 2

(4) Both molecularity and order = 2

Sol. Answer (2, 3)

The reaction given is

$A_2 + B_2 \rightleftharpoons 2AB$

Mechanism

$A_2 \rightleftharpoons A + A$ (fast)

$A + B_2 \rightarrow AB + B$ (Slow reaction)

$A + B \rightarrow AB$ (Fast reaction)

Applying the rate equation w.r.t. slow reaction

$$\frac{dx}{dt} = k\,[A]\,[B_2] \qquad \ldots(i)$$

and we can also write

$$K_c = \frac{[A]^2}{[A_2]}$$

$\therefore$ $[A] = \{K_c[A_2]\}^{1/2}$ …(ii)

Substituting eq. (ii) in eq. (i)

$$\frac{dx}{dt} = K\,\{K_c[A_2]\}^{1/2}[B_2]$$

$$\Rightarrow \frac{dx}{dt} = K'\,[A_2]^{1/2}\,[B_2]$$

Here $K' = K.K_c^{1/2}$

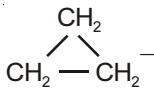
$\therefore$ According to above rate law,

$$\text{Order} = 1+\frac{1}{2} = 3/2$$

And since two reactants are involved hence molecularity is equal to 2.

6. Which of the following are unimolecular?

(1) $O_3 \longrightarrow O_2 + [O]$

(2)  $\longrightarrow CH_3 - CH = CH_2$

(3) $NO + O_3 \longrightarrow NO_2 + O_2$

(4) $O + NO + N_2 \longrightarrow NO_2 + N_2$

Sol. Answer (1, 2)

Fact.

7. For the reaction $A \longrightarrow B$, the rate law is $R = k[A]^2$, which of the following statements are correct?

(1) The reaction follows first order kinetics

(2) The $t_{1/2}$ of the reaction depends upon initial concentration of reactant

(3) The unit of rate constant litre $mole^{-1}$ s^{-1}

(4) K is constant for the reaction at all temperature

Sol. Answer (2, 3)

The given reaction is $A \rightarrow B$. Rate law is given as

$\frac{dx}{dt} = K[A]^2$

It indicates that reaction follows II order kinetics.

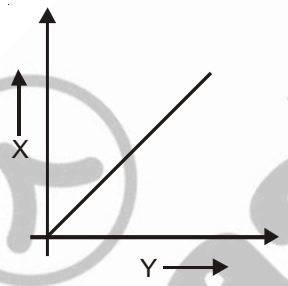
$t_{1/2} = \frac{1}{K[A]_0}$ hence half life is inversely related to concentration,

K has units = $\frac{M}{s.M^2} \Rightarrow \frac{1}{M.s}$

$\frac{1 \times \text{litre}}{\text{moles} \times s}$ = litre $mol^{-1}s^{-1}$

and it depends upon temperature.

8. The plot given is not possible for



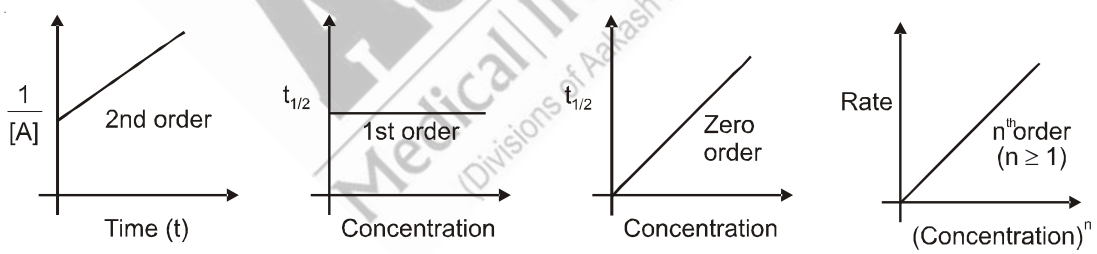
(1) 2nd order reaction $\rightarrow \frac{1}{[A]}$ vs. time

(2) 1st order reaction $\rightarrow t_{1/2}$ vs. concentration

(3) Zero order reaction $\rightarrow t_{1/2}$ vs. concentration

(4) n^{th} order reaction $\rightarrow$ rate vs. concentration

Sol. Answer (1, 2, 4)



9. Incorrect statement(s) among the following is/are

(1) An autocatalytic reaction is catalysed by one of the reactants

(2) A catalyst never enters into chemical reactions

(3) An elementary exothermic reaction (step) can have zero activation energy

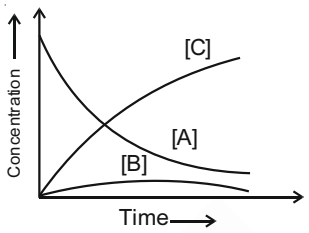
(4) An elementary endothermic reaction can have zero activation energy

Sol. Answer (1, 2, 3, 4)

Fact.

10. Consider the following first order sequential reaction $A \xrightarrow{k_1} B \xrightarrow{k_1'} C$

If variation of concentration with time is given



On the basis of above information, select the correct statement(s).

(1) $k_1 >> k_1'$

(2) $k_1 << k_1'$

(3) Concentration of [B] at any instant is $[B] \simeq \frac{k_1}{k_1'}[A_0]e^{-k_1 t}$. Where $[A_0]$ is initial concentration of A

(4) Concentration of [C] at any time t is $[C]_t \simeq k_1 A_0 e^{-k_1 t}$

Sol. Answer (2, 3)

From the graph we can say $\frac{dB}{dt} \simeq 0$ and it is only possible when $k_1' >> k$

11. Which of the following statements is/are correct regarding catalyst?

(1) Increases the average kinetic energy of reacting molecules

(2) Decreases or increases the activation energy

(3) Alters the reaction mechanism

(4) Increases the frequency of collisions of reacting molecules

Sol. Answer (2, 3)

A catalyst alters the mechanism and consequently decreases or increases the activation energy.

It does not increase the frequency of collisions, since it depends upon temperature.

12. For a first order reaction

(1) The degree of dissociation is equal to $1 - e^{-kt}$

(2) The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

(3) The time taken for completion of 75% reaction is twice the $t_{1/2}$ of the reaction

(4) A plot of reciprocal of concentration of the reactant versus time gives a straight line

Sol. Answer (1, 2, 3)

For I-order reaction we can write

$$K = \frac{1}{t} \ln\left(\frac{1}{1-x}\right)$$

$-Kt = \ln (1 - x)$

$e^{-Kt} = (1 - x) \Rightarrow x = 1 - e^{-Kt}$

$\therefore$ Degree of dissociation is $(1 - e^{-Kt})$

In the equation $K = A.e^{\frac{-Ea}{RT}}$

'K' has same dimensions as 'A' as $[\text{time}]^{-1}$.

For $t_{1/2}$ of I-order

$$(t_{1/2})_I = \frac{\ln 2}{K}$$

For 75% completion

$$t = \frac{1}{K} \ln \left(\frac{a}{a - \frac{75\,a}{100}} \right) = \frac{\ln 4}{K}$$

$$\therefore \quad t = \frac{2\ln 2}{K} = 2t_{1/2}$$

$\frac{1}{[A]_t}$ versus t graph gives a straight line for II-order and not for I-order.

13. Which of the following statement(s) is/are correct?

(1) A plot of log k_p versus $\frac{1}{T}$ is linear

(2) A plot of log [x] versus time is linear for zero order reaction

(3) A plot of P versus $\frac{1}{T}$ is linear at constant volume

(4) A plot of P versus $\frac{1}{V}$ is linear at constant temperature and number of moles

Sol. Answer (1, 4)

According to Boyle's law

$P \propto \frac{1}{V}$ (at constant T and no. of moles) $\Rightarrow P = \frac{K}{V}$

Between P and $\left(\frac{1}{V}\right)$ the graph will be straight line

P versus T graph will be straight line. For zero order x = kt

i.e., x versus t graph gives straight line and not log x versus t.

$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H}{2.303\,K} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Hence the graph between log K_p versus $\frac{1}{T}$ will be linear.

14. Activity of a radioactive sample changes from 1600 to 200 dps in 12 sec. Select the correct statement about this radioactivity process.

(1) Activity become 400 dps after 8 sec of start of process

(2) Half life of the sample is 2 sec

(3) Decay constant of the sample is 0.3465 sec^{-1}

(4) Activity becomes 800 dps after 4 sec of starting

Sol. Answer (1, 4)

Activity $\propto$ (N)

$1600 \rightarrow 800 \rightarrow 400 \rightarrow 200$

12 sec = $3t_{1/2}$

$t_{1/2}$ = 4 s

$$\lambda = \frac{0.693}{t_{1/2}} = 0.71 \text{ sec}^{-1}$$

15. A catalyst lowers the activation energy of forward reaction . It also changes the activation energy of backward reaction by an amount

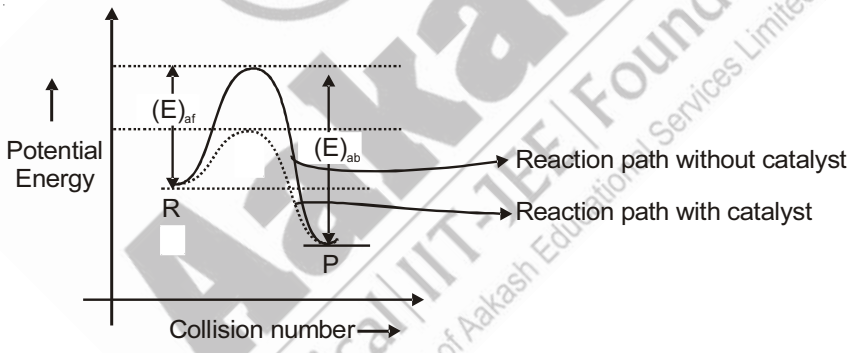
(1) Equal to that of forward reaction

(2) Twice to that of forward reaction

(3) Determined only by average energy of products

(4) Determined by average energy of products relative that of reactants

Sol. Answer (1)



16. Correct statement(s) among the following is/are

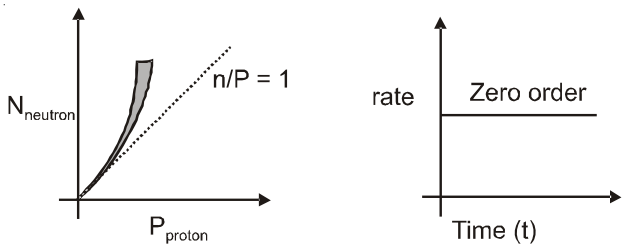
(1) A plot of number of neutrons vs. number of protons is linear when number of protons are very low

(2) Plot is increasing for log[A] vs. time for first order reaction

(3) Decreasing plot for $t_{1/2}$ vs. concentration for zero order reaction

(4) Constant rate for zero order

Sol. Answer (1, 4)



17. Nuclear reactions accompanied with the emission of neutron(s) are

(1) $^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}_{15}P^{30}$ (2) $^{12}_{6}C + {}_{1}H^{1} \longrightarrow {}_{7}N^{13}$

(3) $^{30}_{15}P \longrightarrow {}^{30}_{14}Si$ (4) $^{241}_{95}Am + {}_{2}He^{4} \longrightarrow {}^{244}_{97}Bk$

Sol. Answer (1, 4)

Applying mass and charge balance

$^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + {}_{0}n^{1}$ $\begin{pmatrix} q = 13+2 = 15+0 \\ m = 27+4 = 30+1 \end{pmatrix}$

$^{12}_{6}C + {}_{1}H^{1} \rightarrow {}_{0}n^{1} + {}_{7}N^{13}$ $\begin{pmatrix} 12+1 \neq 13+1 \\ 6+1 = 7+0 \end{pmatrix}$

$^{30}_{15}P + {}^{30}_{14}Si + {}_{-1}e^{0} + {}_{0}n^{1}$ $\begin{pmatrix} m = 30 \neq 30+1 \\ q = 15 \neq 14-1 \end{pmatrix}$

$^{241}_{95}Am + {}^{4}_{2}He \rightarrow {}^{244}_{97}Bk + {}_{0}n^{1}$ $\begin{pmatrix} 241+4 = 244+1 \\ 95+2 = 97 \end{pmatrix}$

18. A radioactive element decays as

$$X \xrightarrow[t_{1/2} = 30 \text{ minute}]{\alpha \text{ decay}} Y \xrightarrow[t_{1/2} = 2 \text{ days}]{(-2\beta)\ \beta \text{ decay}} Z$$

Which of the following statements about this decay process is/are correct?

(1) After two hours, less than 10% of the initial X is left

(2) Maximum amount of Y present at any time before 30 minute is less than 50% of the initial amount of X

(3) Atomic number of X and Y are same

(4) Mass number of X and Y are same

Sol. Answer (1, 2)

$$(X) \xrightarrow{\alpha\text{–decay}} (Y) \xrightarrow{-2\beta} (Z)$$

$t_{1/2}$ = 30 minute $t_{1/2}$ = 2 days

When above decays take place

$$^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}Y \xrightarrow{-2\beta^{-}} {}^{A-4}_{Z}Z$$

After 2 hrs

$$N_t = N_0\left(\frac{1}{2}\right)^{x} = N_0\left(\frac{1}{2}\right)^{4} = \left(\frac{N_0}{16}\right) < 10\%$$

Hence (Y) amount at any time before 30 minute is less than 50% as (Y) disintegrate to give Z also.

19. Which of the following statements is/are correct?

(1) Nuclear isomers contain same number of protons and neutrons

(2) The decay constant is independent of the amount of substance taken

(3) The decay constant is independent of temperature and pressure

(4) The value of decay constant generally increases with temperature since radioactive reaction obeys first order kinetics

Sol. Answer (1, 2, 3)

For radioactivity, which follows first order kinetics

$\lambda = \frac{\ln 2}{t_{1/2}}$ hence, it is independent of the amount of substance taken. And λ (or radioactivity) is independent of external factors like temperature and pressure.

Nuclear isomers contains same number of protons and neutrons.

20. The gas phase decomposition of acetic acid at 1189 K to form ketene ($CH_2 = C = O$) proceeds as

$CH_3COOH \longrightarrow CH_2 = C = O + H_2O$

The rate constant for above decomposition is 4.65 sec^{-1}. However at the given temperature another competing reaction

$CH_3COOH \rightarrow CH_4 + CO_2$ with a rate constant of 3.74 s^{-1} comes into picture

Select the correct statement(s).

(1) Maximum % yield of ketene ($H_2C = C = O$) is more than 50%

(2) Maximum % yield of CH_4 is more than 50%

(3) Maximum % yield of ketene (CH_2CO) is more than maximum % yield of CH_4

(4) Maximum % yield of ketene (CH_2CO) is less than maximum % yield of CH_4

Sol. Answer (1, 3)

$$\% \text{ yield of ketene} = \frac{k_2}{k_1 + k_2}\left(1 - e^{-(k_1 + k_2)t}\right) \times 100$$

For maximum yield

$$1 - e^{-(k_1 + k_2)t} = 1$$

$$\% \text{ yield of ketene} = \frac{k_2}{k_1 + k_2} = \frac{4.65 \times 100}{3.74 + 4.65}$$

$$= 55.5\%$$

$$\% \text{ yield and } CH_4 = \frac{k_2}{k_1 + k_2} = \frac{3.74}{4.65 + 3.74}$$

$$= 44.57\%$$

21. The process(es) in which neutrino is produced is/are (every process occurs in single step)

(1) $^{64}Cu \rightarrow {}^{64}Ni$ (2) $^{23}Na \rightarrow {}^{23}Mg$ (3) $^{238}U \rightarrow {}^{234}Th$ (4) $^{14}O \rightarrow {}^{14}N$

Sol. Answer (1, 4)

When 1 proton convert into neutron then β^+ as well as neutrino is produced.

22. Activity of a radioactive sample decreases from A_1 to A_2 in a certain time interval. If half life of the sample is T, then the number of nucleus decayed within the time interval 'T' is ('λ' is decay constant)

(1) $\frac{\ln 2}{T}(A_1 - A_2)$ (2) $\frac{T}{\ln 2}(A_1 - A_2)$ (3) $\frac{1}{\lambda}(A_1 - A_2)$ (4) $T \ln 2 (A_1 - A_2)$

Sol. Answer (2, 3)

$A_1 = \lambda N_1$

$A_2 = \lambda N_2$

$\Delta_n = N_1 - N_2 = \frac{1}{\lambda}(A_1 - A_2)$

$\frac{T}{\ln 2}(A_1 - A_2)$

23. Activity of charcoal A is 8 times greater than that of charcoal B. Select the correct statement if Half life of ^{14}C is 5600 years

(1) B is 16800 years older than A (2) B is 11200 years older than A

(3) A is 16800 years older than B (4) A is 11200 years older than B

Sol. Answer (1)

Activity of B is $\frac{1}{8}$ times of A means ^{14}C of B is decayed so B is older.

Activity $\propto$[N]

Number of nucleus in B = $\frac{1}{8}$ time of nucleus of A

24. Consider the given elementary reaction

A $\longrightarrow$ Product

Half life of reaction is Y sec when reaction occurs in absence of catalyst while half life is X sec when reaction occurs in presence of catalyst. Select the correct statement(s) if temperature of reaction remain constant.

(1) X must be greater than Y

(2) X must be less than Y

(3) Rate constant in presence of catalyst is more as compared to rate constant in absence of catalyst

(4) Relation between X and Y cannot be determined without the knowledge of initial concentration

Sol. Answer (2, 3)

If reaction is elementary then it is first order.

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

$k = A\, e^{-E_a/RT}$

Catalyst increase the k so half life decreases.

SECTION - C

Linked Comprehension Type Questions

Comprehension-I

The following data are for the reaction A + B $\longrightarrow$ Products

Concentration [A] (M)	Concentration [B] (M)	Initial rate (mol $L^{-1}s^{1}$)
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.5	1.0×10^{-2}
0.5	0.2	1.0×10^{-2}

1. What is the order with respect to A and B for the reaction respectively?

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

Sol. Answer (3)

2. Calculate the rate constant (mole L^{-1} s^{-1})

(1) 4×10^{-2} (2) 4×10^{-4} (3) 1.6×10^{-3} (4) 1×10^{-2}

Sol. Answer (1)

3. Determine the reaction rate when [A] and [B] are 0.2 M and 0.35 M, respectively.

(1) 1×10^{-2} (2) 1.6×10^{-3} (3) 4×10^{-4} (4) 1×10^{-4}

Sol. Answer (2)

Comprehension-II

According to Soddy Fajan Law

"When an α-particle is emitted, the daughter element has atomic number 2 units less than that of parent element. It is consequently displaced two places (groups) to the left in the periodic table. When a β-particle is emitted, the daughter element has an atomic number 1 unit higher than that of parent element. It is consequently displaced one place (group) to the right in the periodic table".

1. Radioactive disintegration of ${}_{88}Ra^{226}$ takes place in the following sequence

$$Ra \xrightarrow{-\alpha} A \xrightarrow{-\alpha} B \xrightarrow{-\alpha} C \xrightarrow{-\beta} D$$

The atomic number and group of D will be respectively

(1) 82, 14 (2) 83, 14 (3) 83, 15 (4) 84, 16

Sol. Answer (3)

$${}_{88}Ra^{226} \rightarrow {}_{2}He^{4} + {}^{222}_{86}A$$

$${}^{222}_{86}A \rightarrow {}_{2}He^{4} + {}^{218}_{84}B$$

$${}^{218}_{84}B \rightarrow {}_{2}He^{4} + {}^{214}_{82}C$$

$${}^{214}_{82}C \rightarrow {}^{214}_{83}D + {}^{0}_{-1}B$$

$\therefore$ Atomic number of D will be 83 and will be lying in group 15.

2. ${}_{90}Th^{234}$ disintegrates to give ${}_{82}Pb^{206}$. The number of α and β-particle emitted in this process will be respectively

(1) 7, 6 (2) 6, 7 (3) 8, 8 (4) 6, 4

Sol. Answer (1)

${}_{90}Th^{234} \rightarrow {}_{82}Pb^{206}$

Since atomic mass decreases from 234 to 206 the difference is 28 and per α-particle emission the mass decreases by 4 units.

$\therefore$ Number of α-particles emitted = $\frac{28}{4} = 7$

Atomic no. decreases by $7 \times 2 = 14$ or it becomes 76.

In the product no. of protons is 82 hence 6β particles are emitted

$\therefore$ No. of α-particles emitted = 7

No. of β-particles emitted = 6

3. Number of neutrons and group number after emission of an α-particle from $_{92}U^{238}$ group III

(1) N =146, group III (2) N = 144, group I

(3) N = 144, group III (4) None of these

Sol. Answer (3)

The given radioactive element is $_{92}U^{238} \rightarrow {}_2He^4 + {}^{234}_{90}X$

$\therefore$ Number of neutrons in X = 234 – 90 = 144

Comprehension-III

Hydrolysis of sucrose ($C_{12}H_{22}O_{11}$), a first order reaction gives glucose ($C_6H_{12}O_6$) and fructose ($C_6H_{12}O_6$).

$$\underset{\text{(Dextro)}}{S} \xrightarrow{H_2O} \underset{\text{(Dextro)}}{G} + \underset{\text{(Laevo)}}{F}$$

The rotation of plane polarised light at different angles by S, G and F is directly proportional to their concentration. Given

Time	0	t	∞
Rotation (S + G + F)	r_0	r_t	r_∞

a = Initial concentration of sucrose.

1. If combined rotation of glucose and fructose is equal to the value of initial rotation, then $\frac{r_0}{r_\infty}$ is equal to

(1) 0 (2) 1 (3) ∞ (4) a

Sol. Answer (2)

$r_1^0 = r_2^0 - r_3^0$

$$\frac{r_0}{r_\infty} = \frac{a\, r_1^0}{a(r_2^0 - r_3^0)} = 1$$

2. If amount of rotation of glucose (per mole) is equal to amount of rotation of fructose (per mole), then $\frac{r_\infty}{r_0}$ is equal to

(1) 0 (2) 1 (3) ∞ (4) a

Sol. Answer (1)

$r_2^0 = r_3^0$

$$\frac{r_\infty}{r_0} = \frac{a(r_2^0 - r_3^0)}{a r_1^0} = 0. (\because \quad r_\infty = 0)$$

3. In previous question, after 30 seconds total rotation is equal to half of initial rotation. Then value of rate constant is (in s^{-1})

(1) ln2 (2) $\frac{30}{\ln 2}$ (3) $\frac{\ln 2}{30}$ (4) 10^{-2}

Sol. Answer (3)

$$k = \frac{1}{30}\ln\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$$

$$\frac{1}{30}\ln\left(\frac{r_0}{r_t}\right) = \frac{1}{30}\ln 2 \left(\because \quad r_t \frac{1}{2} r_0\right)$$

SECTION - D

Matrix-Match Type Questions

1. Match the following :

Column-I	Column-II
(A) $_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + ...$	(p) $_2He^4$
(B) $_6C^{12} + ... \longrightarrow {}_5B^{10} + {}_2He^4$	(q) $_0n^1$
(C) $_7N^{14} + ... \longrightarrow {}_8O^{17} + {}_1H^1$	(r) $_1D^2$
(D) $_{20}Ca^{40} + ... \longrightarrow {}_{19}K^{37} + {}_2He^4$	(s) $_1H^1$

Sol. Answer A(q), B(r), C(p), D(s)

Applying the mass –balance and charge balance

The reactions can be written as

(A) $_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1$ $\begin{pmatrix}\text{mass} = 13\\ \text{charge} = 6\end{pmatrix}$

(B) $_6C^{12} + {}_1D^2 \rightarrow {}_5B^{10} + {}_2He^4$ $\begin{pmatrix}\text{mass} = 12+2 = 10+4\\ \text{charge} = 6+1 = 5+2\end{pmatrix}$

(C) $_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1$ $\begin{pmatrix}\text{mass} = 14+4 = 17+1\\ \text{charge} = 7+2 = 8+1\end{pmatrix}$

(D) $_{20}Ca^{40} + {}_1H^1 \rightarrow {}_{19}K^{37} + {}_2He^4$ $\begin{pmatrix}\text{mass} = 40+1 = 4+37\\ \text{charge} = 20+1 = 19+2\end{pmatrix}$

2. Match the following :

Column-I	Column-II
(A) Half life of zero order reaction	(p) $\frac{1}{k.a}$
(B) Half life of first order reaction	(q) 2 – 3
(C) Temperature coefficient	(r) $\frac{0.693}{k}$
(D) Half life of second order reaction	(s) $\frac{a}{2k}$

Sol. Answer A(s), B(r), C(q), D(p)

Half life for the reaction is inversely related to $(a)^{n-1}$ where 'n' is the order of the reaction

$\therefore$ For I-order; $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$

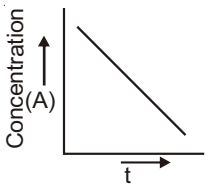
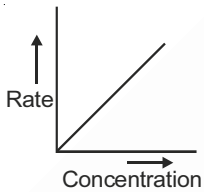
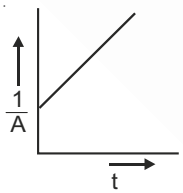
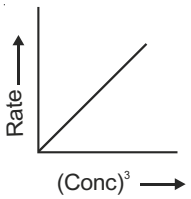
for zero order; $t_{1/2} = \frac{a}{2k}$

for II-order reaction

$t_{1/2} = \frac{1}{k.a}$

The temperature coefficient of reaction is the ratio of rate constants differing by a temperature of 10ºC.

3. Match the following :

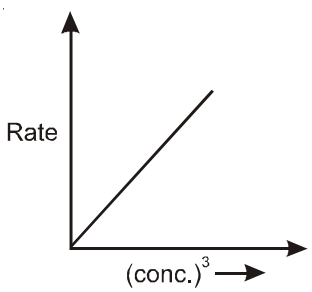
Column-I	**Column-II**
(A) 	(p) 3
(B) 	(q) 2
(C) 	(r) 1
(D) 	(s) 0

Sol. Answer A(s), B(r), C(q), D(p)

For III-order reaction we can write

$\frac{dx}{dt} = k\,(a - x)^3$

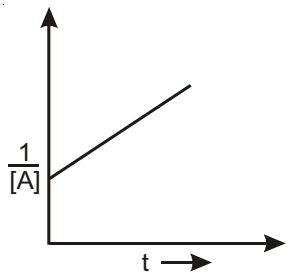
The graph will be straight line between $\left(\frac{dx}{dt}\right)$ and $(a - x)^3$ passing through the origin.



For II order, the equation is,

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

The graph between $\frac{1}{[A]_t}$ versus t is a straight line having +ve slope and intercept = $\frac{1}{[A]_0}$.



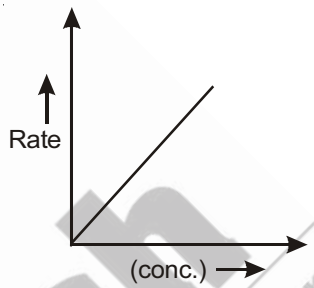
∴ The graph is for II-order reaction

For I-order reaction the equation can be written as

$$\frac{dx}{dt} = k(a - x)$$

Hence $\left(\frac{dx}{dt}\right) \propto (a - x)$

∴ The graph for I-order is



For zero-order reaction, the concentration decreases as time progresses at constant rate.

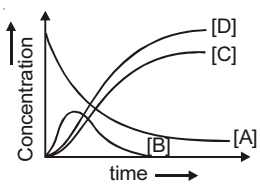
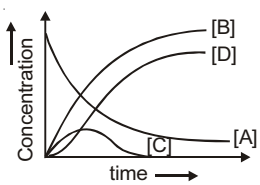
∴ Graph will be

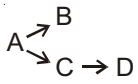
4. Match the following :

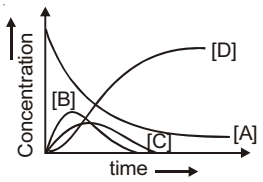
Column I	**Column II**
(A) $\frac{K_{T+10}}{K_T}$	(p) Arrhenius equation
(B) $e^{-E_a/RT}$	(q) Temperature coefficient
(C) Rate = K [Reactant]^n	(r) Boltzmann factor
(D) $k = Ae^{-E_a/RT}$	(s) Rate law expression

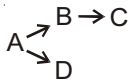
Sol. Answer A(q), B(r), C(s), D(p)

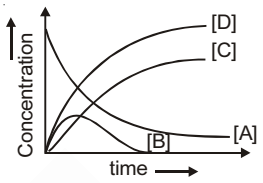
5. Match the following :

Column I	**Column II**
(A) $A \rightarrow B \rightarrow C \rightarrow D$	(p) 
(B) $A \rightarrow B \rightarrow D$ $\downarrow$ C	(q) 

(C) 

(r) 

(D) 

(s) 

Note : *Assume that all reactions are moderately fast reactions.*

Sol. Answer A(r), B(p), C(q), D(s)

SECTION - E

Assertion-Reason Type Questions

1. STATEMENT-1 : Rate of Radioactive decay is independent of external factors (like pressure, temperature).

   and

   STATEMENT-2 : Radioactive decay follows second order kinetics.

Sol. Answer (3)

Radioactivity is a nuclear phenomenon and is independent of external factors like temperature, pressure etc.

Radioactivity follows first order kinetics and number of nuclei at any time 't' is given by

$$N_t = N_0\, e^{-\lambda t}$$

$\therefore$ Statement (1) is correct but statement (2) is false.

2. STATEMENT-1 : Acidic hydrolysis of ester is an example of pseudounimolecular reaction.

   and

   STATEMENT-2 : Molecularity of acidic hydrolysis of ester is one.

Sol. Answer (3)

For acidic hydrolysis the reaction is

$$CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3CH_2OH + CH_3COOH$$

$$\frac{dx}{dt} = K[CH_3COOCH_2CH_3]$$

but two species are involved in the reaction. Hence, it is bimolecular. These reactions are pseudo-unimolecular reactions.

$\therefore$ Statement (1) is true but statement (2) is false.

3. STATEMENT-1 : Half life of first order reaction is independent of initial concentration of reactants.

   and

   STATEMENT-2 : Half life of first order reaction is inversely proportional to the rate constant.

Sol. Answer (2)

Half life for I-order reaction is given as

$t_{1/2} = \frac{\ln 2}{K}$ (independent of initial concentration & inversely proportional to K)

∴ Statement (1) & (2) both are correct but statement (2) is not the correct explanation of statement (1).

4. STATEMENT-1 : Activation energy of forward reaction (E_{af}) is greater than activation energy of backward reaction (E_{ab}) for an endothermic reaction.

and

STATEMENT-2 : Rate constant for a first order reaction is dependent on temperature.

Sol. Answer (2)

ΔH for the reversible reaction is given by

$(\Delta H) = (E_a)_f - (E_a)_b$

For endothermic reaction $\Delta H > 0$ $\therefore (E_a)_f - (E_a)_b > 0$ or $(E_a)_f > (E_a)_b$

The rate constant for the first order reaction is given by

$K = A.e^{-E_a/RT}$

Hence, statement (2) is not the correct explanation.

5. STATEMENT-1 : Positive catalysts lowers the activation energy of the reaction.

and

STATEMENT-2 : Heat of reaction is equal to the difference between activation energies for forward and backward reactions.

Sol. Answer (2)

Only a positive catalyst lowers the activation energy and increases the rate of reaction.

And $(\Delta H) = (E_A)_f - (E_A)_b$

∴ Statement (2) is not the correct explanation because the catalyst provides an alternate mechanism for the conversion of reactants to products.

6. STATEMENT-1 : The rate of reaction always depends on the concentration of reactants.

and

STATEMENT-2 : Order of reaction of a component can be negative with respect to reaction.

Sol. Answer (4)

The rate of reaction also depends upon temperature and order of the reaction can be positive, negative, zero or even fractional.

7. STATEMENT-1 : The rate of reaction increases generally by 2 to 3 times for every 10°C rise in temperature.

and

STATEMENT-2 : Increase in temperature increases the collision frequency.

Sol. Answer (2)

The rate of reaction generally increases the rate by 2 times to 3 times. We also define

$$\frac{K_{T+10}}{K_T} = T_C \text{ (Temp. coefficient)}$$

and with the increase in temperature collision frequency increases as more molecules cross the energy barrier and acquire activation energy.

8. STATEMENT-1 : For a first order reaction, rate of the reaction doubles as concentration of reactant gets doubled.

and

STATEMENT-2 : Rate is directly proportional to concentration of reactant.

Sol. Answer (1)

Rate = k [reactant].

9. STATEMENT-1 : The pseudo order of reaction $CH_3COOC_2H_5 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$ is 2.

and

STATEMENT-2 : The molecularity of given reaction is two.

Sol. Answer (4)

Order of reaction is 1 (pseudo-order)

10. STATEMENT-1 : If activation energy is zero, then temperature will have no effect on rate constant.

and

STATEMENT-2 : Lower the activation energy, faster is the reaction.

Sol. Answer (2)

$k = Ae^{-E_a/RT}$

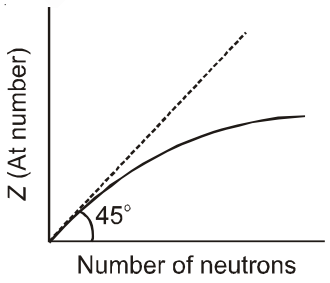
For $E_a = 0 \Rightarrow k = A$

11. STATEMENT-1 : The plot of atomic number (*y*-axis versus number of neutrons (*x*-axis) for stable nuclei shows a curvature towards *x*-axis from the line of 45° slope as the atomic number is increased.

and

STATEMENT-2 : Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

Sol. Answer (2)



Elements with higher atomic number are more stable if they have slight excess of neutron as this increase the attractive force and also reduces repulsion between protons.

SECTION - F

Integer Answer Type Questions

1. Two radioactive elements X and Y have half lives of 100 and 50 minutes respectively. Initial sample of both the elements have same number of atoms. Find the ratio of remaining no. of atoms of X and Y after 200 minutes.

Sol. Answer (4)

After 200 minutes,

Remaining about of $X = \frac{a}{2^2}$

Remaining about of $Y = \frac{a}{2^4}$

$\Rightarrow$ Ratio = $\frac{2^4}{2^2} = 4$

2. H_2O and O atom react in upper atmosphere bimolecularly to form two OH radicals. ΔH for the reaction is 72 kJ at 500 K and energy of activation is 77 kJ / mol. Estimate E_a (kJ/mol) for bimolecular recombination of two OH radicals to form H_2O & O atom.

Sol. Answer (5)

$H_2O + O \xrightarrow{E_a} 2OH \qquad \Delta H = 72\ kJ$

$2OH \xrightarrow{E_b} H_2O + O \qquad \Delta H = -72\ kJ$

Also, $E_a - E_b = \Delta H$

$\Rightarrow E_b = 5$ kJ/mol

3. For the reaction given below, the rate expression is given as : $RX + OH^- \rightarrow ROH + X^-$

$$\text{rate} = \underbrace{4.7\times10^{-5}[RX][OH^-]}_{S_N2} + \underbrace{0.24\times10^{-5}[RX]}_{S_N1}$$

What percentage of RX reacts by the S_N2 mechanism when $[OH^-] = 0.001M$?

Sol. Answer (2)

$$\%\ \text{rate of } S_N2 = \left[\frac{r_{S_N2}}{r_{S_N1} + r_{S_N2}}\right]\times100 = \frac{4.7\times10^{-5}[RX][OH^-]}{4.7\times10^{-5}[RX][OH^-] + 0.24\times10^{-5}[RX]}\times100 \simeq 2.1 \left(\because [OH^-] = 0.001M\right)$$

4. The rate of a certain reaction depends on concentration according to the equation :

$$-\frac{dC}{dt} = \frac{K_1C}{1+K_2C}$$

What will be the order of reaction, when concentration C is very low?

Sol. Answer (1)

$\because$ C is low, then $1+k_2C \approx 1$

$\Rightarrow \quad -\frac{dC}{dt} = k_1C$

Hence, reaction is of 1st order.

5. For a first order reaction, $t_{99.99\%} = y \times t_{90\%}$. Find the value of y.

Sol. Answer (4)

$$t_{99.99\%} = \frac{2.303}{k}\log_{10}\frac{1}{10^{-4}} = 4\times\frac{2.303}{k}$$

$$t_{90\%} = \frac{2.303}{k}\log_{10}\frac{1}{10^{-1}} = \frac{2.303}{k}$$

6. Consider the following first order gaseous reaction in a constant volume container.

$$N_2O(g)\longrightarrow N_2(g)+\frac{1}{2}O_2(g)$$

If initially only $N_2O(g)$ is present and total pressure at time t = 0 and after time 't' are P_i and P respectively, then the rate constant is expressed as $K=\frac{1}{t}\ln\left(\frac{P_i}{xP_i-yP}\right)$, then $x^3 + y^3$ is

Sol. Answer (35)

$$N_2O(g)\longrightarrow N_2(g)+\frac{1}{2}O_2(g)$$

$$K=\frac{1}{t}\ln\left(\frac{P_i}{3P_i-2P}\right)$$

$$N_2O(g)\longrightarrow N_2(g)+\frac{1}{2}O_2(g)$$

P_i	0	0
$P_i - p$	p	$\frac{p}{2}$

$$P = P_i + \frac{p}{2}$$

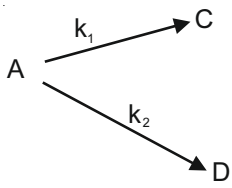
$$2P - 2P_i = p$$

p_{N_2O} at $t = P_i - (2P - 2P_i)$

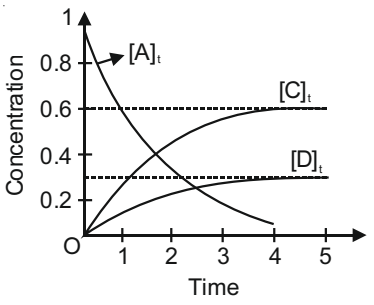
$= 3P_i - 2P$

$$K = \frac{1}{t}\ln\left(\frac{P_i}{3P_i-2P}\right)$$

7. Consider the first order parallel reaction.



The graph of concentration versus time is given



From the above information compute the value of $5(k_1/k_2)$.

Sol. Answer (10)

$$\frac{[C]}{[D]} = \frac{k_1}{k_2}$$

$$\frac{[C]}{[D]} = 2$$

so, $2k_2 = k_1$

8. CH_3CHO is thermally decomposed to CH_4 and CO as

$$CH_3CHO \longrightarrow CH_4 + CO$$

and rate of reaction in terms of CH_4 is $\frac{d[CH_4]}{dt} = K[CH_3CHO]^{\frac{3}{2}}$

[K is overall rate constant].

Mechanism:

Step (I) $CH_3CHO \xrightarrow{K_1} \dot{C}H_3 + \dot{C}HO$

Step (II) $\dot{C}H_3 + CH_3CHO \xrightarrow{K_2} CH_4 + \dot{C}H_2CHO$

Step (III) $\dot{C}H_2CHO \xrightarrow{K_3} \dot{C}H_3 + CO$

Step (IV) $2\dot{C}H_3 \xrightarrow{K_4} CH_3CH_3$

The pre-exponential factor (A) for step I, II, III and IV are 10^{10}, 10^6, 10^5 and 5×10^3 respectively. The pre-exponential factor of overall reaction is 10^x. The value of x is (use steady state approximation)

Sol. Answer (9)

$$\text{Rate} = K_2\left(\frac{K_1}{2K_4}\right)^{\frac{1}{2}}[CH_3CHO]^{\frac{3}{2}}$$

$$\text{so, } K = Ae^{-\frac{E_a}{RT}} = A_2e^{-\frac{E_2}{RT}} \times \left(\frac{A_1e^{-\frac{E_1}{RT}}}{2A_4e^{-\frac{E_a}{RT}}}\right)^{\frac{1}{2}}$$

$$A = A_2\left(\frac{A_1}{2A_4}\right)^{\frac{1}{2}}$$

Rate of reaction:

$$\frac{d[CH_4]}{dt} = K_2[\dot{C}H_3][CH_3CHO]$$

Now, by steady state approximation

$$\frac{d[\dot{C}H_3]}{dt} = 0 = K_1[CH_3CHO] - K_2[\dot{C}H_3][CH_3CHO] + K_3[\dot{C}H_2CHO] - 2K_4[\dot{C}H_3]^2 \quad ...(i)$$

$$\frac{d[\dot{C}H_2CHO]}{dt} = 0 = K_2[\dot{C}H_3][CH_3CHO] - K_3[\dot{C}H_2CHO] \quad ...(ii)$$

$$\text{so, } [\dot{C}H_3] = \left(\frac{K_1}{2K_4}[CH_3CHO]\right)^{\frac{1}{2}} \text{ \{from (i) and (ii)\}}$$

$$\frac{d(CH_4)}{dt} = K_2\left[\frac{K_1}{2K_4}[CH_3CHO]\right]^{\frac{1}{2}}[CH_3CHO] = K_2\left(\frac{K_1}{2K_4}\right)^{\frac{1}{2}}[CH_3CHO]^{\frac{3}{2}}$$

$$\text{so } K = K_2\left(\frac{K_1}{2K_4}\right)^{\frac{1}{2}}$$

$$A = A_2\left(\frac{A_1}{2A_4}\right)^{\frac{1}{2}}$$

$$A = 10^6\left(\frac{10^{10}}{2\times5\times10^3}\right)^{\frac{1}{2}} = 10^6\times10^3 = 10^9.$$

9. The rate constant for the decomposition of a certain substance is 1.70×10^{-2} dm^3 mol^{-1} sec^{-1} at 27°C and 2×10^{-2} dm^3 mol^{-1} sec^{-1} at 37°C. If order of reaction is x and Arrhenius parameter of reaction is y dm^3 mol^{-1} sec^{-1}, then $\frac{y\times1000}{43x}$ is (Given, ln(1.176) = 0.162, R = 8.3 J/mol K, $e^{4.86}$ = 129)

Sol. Answer (30)

x = 2, from units of k.

$$\ln\left(\frac{2}{1.7}\right) = \frac{E_a}{8.3}\times\frac{10}{310\times300}$$

E_a = 12504.78 J/mol

$$A = ke^{E_a/RT}$$

$$\exp\frac{E_a}{RT} = \exp\left(\frac{12504.78}{310\times 8.3}\right) = 129$$

$$y = A = \exp\left(\frac{E_a}{RT}\right)\cdot k = 129 \times 2 \times 10^{-2}$$

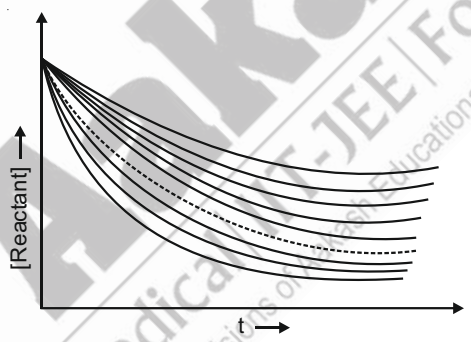
$= 2.58\ dm^2\ mol^{-1}\ sec^{-1}$

$$\frac{2.58\times 1000}{43\times 2} = 30$$

10. Consider the following first order reaction in which initial concentration of each reactant is 1 M.

Reaction number	Reaction	Half life	Rate constant
1	A ⟶ B	50	k_1
2	C ⟶ D	32	k_2
3	X ⟶ Y	43	k_3
4	Z ⟶ W	96	k_4
5	M ⟶ N	65	k_5
6	P ⟶ Q	60	k_6
7	E ⟶ F	89	k_7
8	H ⟶ G	21	k_8
9	T ⟶ R	103	k_9

On the basis of this information, a graph of [reactant] versus t is drawn for the above reactions.



What is the half life of the reaction for which the curve is represented by a dotted line?

Sol. Answer (50)

As value of k increase, concentration decrease more sharply.

11. Consider the reaction.

A ⟶ B

The concentration of A at different times were monitored and the following table was obtained.

t(min)	0	5	10	15	20
Concentration	0.493	0.458	0.423	0.388	0.353

If the rate of the reaction at t = 20 minute is R $\frac{mol}{L\ minute}$, then the value of 1000R is

Sol. Answer (7)

$A_t = A_0 - kt$

$\Rightarrow k = \frac{A_0 - A_t}{t}$

$\therefore k_1 = \frac{0.493 - 0.458}{5}, k_2 = \frac{0.493 - 0.423}{10}$

$k_1 = k_2 = 0.007$

$\therefore 1000k = 7$

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