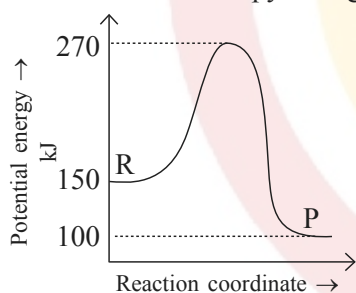


Section A

● Choose correct answer from the given options. [Each carries 1 Mark]

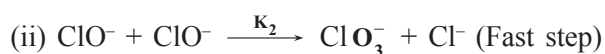
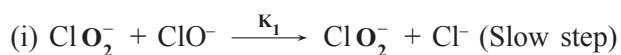
[10]

- The incorrect statement among the following is :
 (A) Actinoid contraction is greater for element to element than Lanthanoid contraction.
 (B) Most of the trivalent Lanthanoid ions are colorless in the solid state.
 (C) Lanthanoids are good conductors of heat and electricity.
 (D) Actinoids are highly reactive metals, especially when finely divided.
- The electronic configurations of Eu (Atomic no. 63), Gd (Atomic NO. 64) and Tb (Atomic NO. 65) are :
 (A) $[\text{Xe}]4f^65d^16s^2$, $[\text{Xe}]4f^75d^16s^2$ and $[\text{Xe}]4f^96s^2$ (B) $[\text{Xe}]4f^65d^16s^2$, $[\text{Xe}]4f^75d^16s^2$ and $[\text{Xe}]4f^85d^16s^2$
 (C) $[\text{Xe}]4f^76s^2$, $[\text{Xe}]4f^75d^16s^2$ and $[\text{Xe}]4f^96s^2$ (D) $[\text{Xe}]4f^76s^2$, $[\text{Xe}]4f^86s^2$ and $[\text{Xe}]4f^85d^16s^2$
- Gadolinium has a low value of third ionisation enthalpy because of _____.
 (A) high electronegativity (B) high basic nature
 (C) Very small size (D) high exchange energy
- For $\text{R} \rightarrow \text{P}$ reaction, following graph is given
 What will be enthalpy change for the given reaction ?



- (A) 120 kJ (B) 50 kJ (C) -50 kJ (D) 170 kJ
- Which is unit of rate constant for the second order reaction ?
 (A) $\text{Mol}^{-1} \text{L s}^{-1}$ (B) $\text{Mol L}^{-1} \text{s}^{-1}$ (C) s^{-1} (D) $\text{Mol}^{-2} \text{L}^2 \text{s}^{-1}$
- Which of the following graph for $\ln k \rightarrow \frac{1}{T}$ is correct ?
 (A) (B) (C) (D)
- For which of the following graph of first order reaction the value of slope will be $\frac{K}{2.303}$
 (A) $\log \frac{[\text{R}]_0}{[\text{R}]} \rightarrow t(\text{Time})$ (B) $\log \frac{[\text{R}]}{[\text{R}]_0} \rightarrow t(\text{Time})$ (C) $\ln \frac{[\text{R}]_0}{[\text{R}]} \rightarrow t(\text{Time})$ (D) $\ln \frac{[\text{R}]}{[\text{R}]_0} \rightarrow t(\text{Time})$
- For a reaction, $K = 4.5 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$. What is order of reaction ?
 (A) Zero (B) Second (C) First (D) Third
- Time required to decompose SO_2Cl_2 to half of its initial amount is 40 minutes. If the decomposition is a first order reaction, what will be the rate constant of the reaction ?
 (A) $2.88 \times 10^{-4} \text{ s}^{-1}$ (B) $2.88 \times 10^{-2} \text{ s}^{-1}$ (C) $1.73 \times 10^{-2} \text{ s}^{-1}$ (D) $1.73 \times 10^{-4} \text{ s}^{-1}$

10. Reaction $3\text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$ occurs in following two steps :



then the rate of given reaction = _____.

(A) $K_1[\text{ClO}^-]$

(B) $K_1[\text{ClO}^-]^2$

(C) $K_2[\text{ClO}_2^-][\text{ClO}^-]$

(D) $K_2[\text{ClO}^-]^3$

Section B

● Write the answer of the following questions. [Each carries 2 Marks]

[2]

1. Explain pseudo first order reaction with example.

Section C

● Write the answer of the following questions. [Each carries 3 Marks]

[12]

2. The following results have been obtained during the kinetic studies of the reaction : $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

Experiment	[A]/	[B]/	Initial rate of formation of D/mol L ⁻¹ min ⁻¹
	mol L ⁻¹	mol L ⁻¹	
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

3. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.
4. The $E^\circ(\text{M}^{2+}/\text{M})$ value for copper is positive (+0.34V). What is possibly the reason for this ? (Hint : consider its high $\Delta_a H^\circ$ and low $\Delta_{\text{hyd}} H^\circ$)
5. What is lanthanoid contraction ? What are the consequences of lanthanoid contraction ?

Section D

● Write the answer of the following questions. [Each carries 4 Marks]

[4]

6. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points :
- (i) electronic configurations
- (ii) oxidation states
- (iii) ionisation enthalpies and
- (iv) atomic sizes.

Section A

● Choose correct answer from the given options. [Each carries 1 Mark]

[10]

1. The incorrect statement among the following is :
- (A) Actinoid contraction is greater for element to element than Lanthanoid contraction.
 (B) Most of the trivalent Lanthanoid ions are colorless in the solid state.
 (C) Lanthanoids are good conductors of heat and electricity.
 (D) Actinoids are highly reactive metals, especially when finely divided.

➡ Ans : (B)

2. The electronic configurations of Eu (Atomic no. 63), Gd (Atomic NO. 64) and Tb (Atomic NO. 65) are :
- (A) $[\text{Xe}]4f^65d^16s^2$, $[\text{Xe}]4f^75d^16s^2$ and $[\text{Xe}]4f^96s^2$ (B) $[\text{Xe}]4f^65d^16s^2$, $[\text{Xe}]4f^75d^16s^2$ and $[\text{Xe}]4f^85d^16s^2$
 (C) $[\text{Xe}]4f^76s^2$, $[\text{Xe}]4f^75d^16s^2$ and $[\text{Xe}]4f^96s^2$ (D) $[\text{Xe}]4f^76s^2$, $[\text{Xe}]4f^86s^2$ and $[\text{Xe}]4f^85d^16s^2$

Ans. (C)

⇨ Eu – $[\text{Xe}]4f^7, 6s^2$

Gd – $[\text{Xe}]4f^7, 5d^1, 6s^2$

Tb – $[\text{Xe}]4f^9, 6s^2$

3. Gadolinium has a low value of third ionisation enthalpy because of _____.

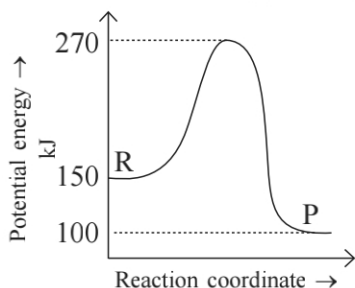
- (A) high electronegativity (B) high basic nature
 (C) Very small size (D) high exchange energy

Ans. (D)

⇨ Gadolinium ($Z = 64$) has configuration $[\text{Xe}]4f^75d^16s^2$. If it loses 3 electrons, it will get extra stable half filled 4f subshell, with $4f^7$ configuration which has high exchange energy.



4. For $R \rightarrow P$ reaction, following graph in given
 What will be enthalpy change for the given reaction ?



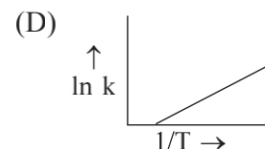
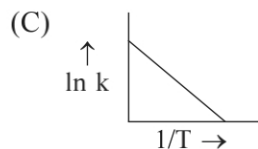
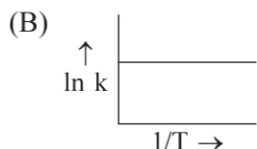
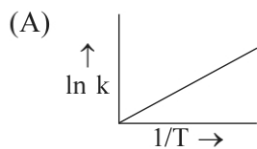
- (A) 120 kJ (B) 50 kJ (C) -50 kJ (D) 170 kJ

➡ Ans : (C)

5. Which is unit of rate constant for the second order reaction ?
- (A) $\text{Mol}^{-1} \text{LS}^{-1}$ (B) $\text{Mol L}^{-1}\text{S}^{-1}$ (C) S^{-1} (D) $\text{Mol}^{-2} \text{L}^2\text{S}^{-1}$

➡ Ans : (A)

6. Which of the following graph for $\ln k \rightarrow \frac{1}{T}$ is correct ?



Ans : (C)

7. For which of the following graph of first order reaction the value of slope will be $\frac{K}{2.303}$

(A) $\log \frac{[R]_0}{[R]} \rightarrow t(\text{Time})$ (B) $\log \frac{[R]}{[R]_0} \rightarrow t(\text{Time})$ (C) $\ln \frac{[R]_0}{[R]} \rightarrow t(\text{Time})$ (D) $\ln \frac{[R]}{[R]_0} \rightarrow t(\text{Time})$

Ans : (A)

8. For a reaction, $K = 4.5 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$. What is order of reaction ?

(A) Zero (B) Second (C) First (D) Third

Ans : (B)

9. Time required to decompose SO_2Cl_2 to half of its initial amount is 40 minutes. If the decomposition is a first order reaction, what will be the rate constant of the reaction ?

(A) $2.88 \times 10^{-4} \text{ s}^{-1}$ (B) $2.88 \times 10^{-2} \text{ s}^{-1}$ (C) $1.73 \times 10^{-2} \text{ s}^{-1}$ (D) $1.73 \times 10^{-4} \text{ s}^{-1}$

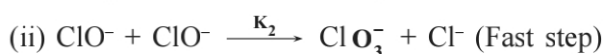
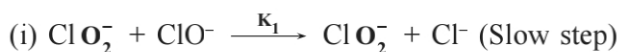
Ans. (A)

$$\begin{aligned} t_{\frac{1}{2}} &= 40 \text{ min} \\ &= 40 \times 60 \\ &= 2400 \text{ Sec} \end{aligned}$$

For First order reaction

$$\begin{aligned} K &= \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{2400} = 0.000288 \\ &= 2.88 \times 10^{-4} \text{ Sec}^{-1} \end{aligned}$$

10. Reaction $3\text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$ occurs in following two steps :



then the rate of given reaction = _____.

(A) $K_1[\text{ClO}^-]$ (B) $K_1[\text{ClO}^-]^2$ (C) $K_2[\text{ClO}_2^-][\text{ClO}^-]$ (D) $K_2[\text{ClO}^-]^3$

Ans : (B)

Section B

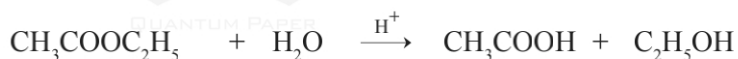
● Write the answer of the following questions. [Each carries 2 Marks]

[2]

1. Explain pseudo first order reaction with example.

⇒ The order of a reaction is sometimes altered by conditions. There are many reactions which obey first order rate law although they are higher order reactions. Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water. In reality, it is second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction. But water is taken in large excess for hydrolysis, therefore, concentration of water is not altered much during the reaction. Thus, the rate of reaction is affected by concentration of ethyl acetate with 10 mol

of water, amounts of the reactants and products at the beginning ($t = 0$) and completion (t) of the reaction are give as under.

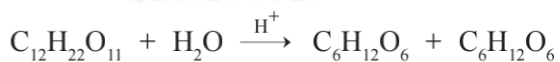


$t = 0$ 0.01 mol 10 mol 0 mol 0 mol

$t = t$ 0 mol 9.99 mol 0.01 mol 0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.



cane sugar Glucose Fructose

$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

Section C

- Write the answer of the following questions. [Each carries 3 Marks] [12]

2. The following results have been obtained during the kinetic studies of the reaction : $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

Experiment	[A]/	[B]/	Initial rate of formation of D/mol L ⁻¹ min ⁻¹
	mol L ⁻¹	mol L ⁻¹	
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

⇒ Suppose,

⇒ Order of reaction with respect to A = x

⇒ Order of reaction with respect to B = y

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

$$\therefore r_1 = k[0.1]^x[0.1]^y = 6.0 \times 10^{-3} \quad \dots \dots (1)$$

$$r_2 = k[0.3]^x[0.2]^y = 7.2 \times 10^{-2} \quad \dots \dots (2)$$

$$r_3 = k[0.3]^x[0.4]^y = 2.88 \times 10^{-1} \quad \dots \dots (3)$$

$$r_4 = k[0.4]^x[0.1]^y = 2.40 \times 10^{-2} \quad \dots \dots (4)$$

Dividing (4) and (1) we get,

$$\Rightarrow \frac{r_4}{r_1} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y} = \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4$$

$$\therefore \frac{r_4}{r_1} = [4]^x = [4]^1$$

$$\therefore x = 1$$

⇒ Order of reaction with respect to A = 1

Dividing (3) and (2) we get,

$$\frac{r_3}{r_2} = \frac{k[0.3]^x[0.4]^y}{k[0.3]^x[0.2]^y} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = 4$$

$$\therefore \frac{r_3}{r_2} = [2]^y = 4 = [2]^2$$

$$\therefore y = 2$$

$$\therefore \text{order of reaction with respect to A} = 1$$

$$\Rightarrow \text{order of reaction with respect to B} = 2$$

$$\Rightarrow \text{overall order of reaction} = 3$$

$$\Rightarrow \therefore \text{rate equation,}$$

$$\Rightarrow \text{Rate} = k[A]^1[B]^2$$

$$\Rightarrow \text{Calculation of rate constant } k$$

$$\Rightarrow \text{From equation (1)}$$

$$\Rightarrow r_1 = k[0.1]^1[0.1]^2 = 6.0 \times 10^{-3}$$

$$k = \frac{6.0 \times 10^{-3}}{[0.1]^1[0.1]^2}$$

$$= \frac{6.0 \times 10^{-3}}{[10]^{-1}[10]^{-2}}$$

$$= 6.0 \text{ mol}^{-2} \text{ L}^{-2} \text{ min}^{-1}$$

3. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

$$\Rightarrow \text{Half-life of } ^{14}\text{C} = 5730 \text{ years.}$$

$$\Rightarrow \text{All radioactive decay follows first order kinetics.}$$

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

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

$$\Rightarrow k = \frac{0.693}{5730} \text{ year}^{-1}$$

$$\Rightarrow \text{For first order reaction.}$$

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

$$\Rightarrow t = \frac{2.303 \times 5730}{0.693} \log \frac{100}{80}$$

$$\Rightarrow t = \frac{2.303 \times 5730}{0.693} \log 1.25$$

$$\Rightarrow t = \frac{2.303 \times 5730}{0.693} \times 0.0969$$

$$\Rightarrow t = 1845.2 \text{ years.}$$

4. The $E^\circ(\text{M}^{2+}/\text{M})$ value for copper is positive (+0.34V). What is possibly the reason for this ?
(Hint : consider its high $\Delta_a H^\circ$ and low $\Delta_{\text{hyd}} H^\circ$)

$$\Rightarrow \text{The } E^\circ(\text{M}^{2+}/\text{M}) \text{ value of a metal depends on the energy changes involved in the following :}$$

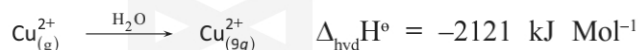
- (1) Sublimation : The energy required for converting one mole of an atom from the solid state to the gaseous state.



(2) Ionization : The energy required to take out electrons from one mole of atoms in the gaseous state.



(3) Hydration : The energy released when one mole of ions are hydrated.



$$\begin{aligned} E^\circ \text{Cu}^{2+}/\text{Cu} &= \Delta_a H^\circ + \Delta_i H^\circ + \Delta_{\text{hyd}} H^\circ \\ &= 339 + 2703 - 2121 \\ &= 1921 \text{ kJ Mol}^{-1} \end{aligned}$$

⇒ Total value of all the enthalpies is positive so reaction is endothermic so $E^\circ \text{Cu}^{2+}/\text{Cu}$ is positive.

5. What is lanthanoid contraction ? What are the consequences of lanthanoid contraction ?

⇒ In a given series decrease in radius with increasing atomic number.

⇒ This is because the new electron enters a d orbital each time the nuclear charge increases by unity. hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases.

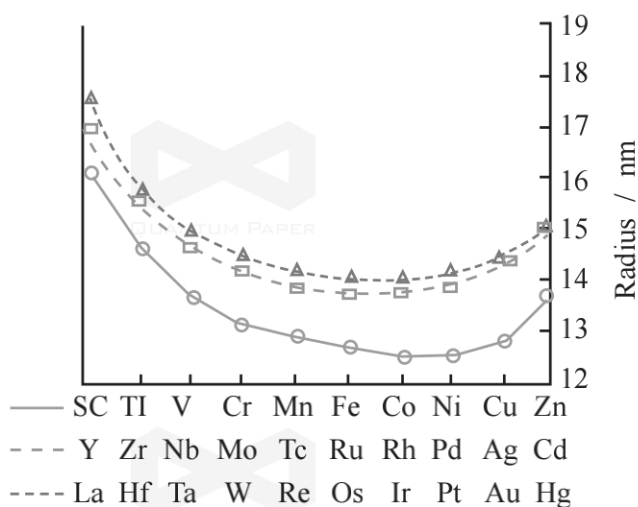
⇒ The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small.

⇒ The curves in Fig. show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series.

⇒ This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin.

⇒ The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction

⇒ The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g. Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.



Trends in atomic radii of transition elements

Section D

● Write the answer of the following questions. [Each carries 4 Marks] [4]

6. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points :
- (i) electronic configurations
 - (ii) oxidation states
 - (iii) ionisation enthalpies and
 - (iv) atomic sizes.
- ⇒ (i) In the 1st, 2nd and 3rd transition series, the 3d, 4d and 5d orbitals are respectively filled.
- ⇒ (ii) In each of the three transition series the number of oxidation states shown by the elements is the maximum in the middle and the minimum at the extreme ends.
- ⇒ However, +2 and +3 oxidation states are quite stable for all elements present in the first transition series. All metals present in the first transition series form stable compounds in the +2 and +3 oxidation states.
 - ⇒ The stability of the +2 and +3 oxidation states decreases in the second and the third transition series, wherein higher oxidation states are more important.
- ⇒ (iii) In each of the three transition series, the first ionisation enthalpy increases from left to right. However, there are some exceptions.
- ⇒ The first ionisation enthalpies of the third transition series are higher than those of the first and second transition series. This occurs due to the poor shielding effect of 4f electrons in the third transition series.
- ⇒ (iv) Atomic size generally decreases from left to right across a period. Now, among the three transition series, atomic sizes of the elements in the second transition series are greater than those of the elements corresponding to the same vertical column in the first transition series.
- ⇒ However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.