# ISC SEMESTER 2 EXAMINATION

# SAMPLE PAPER - 3

# CHEMISTRY PAPER 1 (THEORY)

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***Maximum Marks: 35***

***Time allowed: One and a half hour***

*Candidates are allowed an additional* **10 minutes** *for* **only** *reading the paper.*

*They must* **NOT** *start writing during this time.*

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***All questions are compulsory***

*All working, including rough work, should be done on the same sheet as, and adjacent to the rest of the answer.*

*Balanced equations must be given wherever possible and diagrams where they are helpful.*

*When solving numerical problems, all essential working must be shown.*

*In working out problems, use the following data:*

*Gas constant R = $1{\cdot}987$ cal $deg^{-1}$ $mol^{-1}$ = $8{\cdot}314$ $JK^{-1}$ $mol^{-1}$ = $0{\cdot}0821$ $dm^3$ atm $K^{-1}mol^{-1}$*

*$1$ l atm = $1$ $dm^3$ atm = $101{\cdot}3$ J. 1 Faraday = 96500 coulombs.*

*Avogadro's number = $6{\cdot}023 \cdot 10^{23}$.*

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## Section-A

**Question 1.**

**Fill in the blanks by choosing the appropriate word(s) from those given in the brackets:**

(activation energy, Threshold energy, increased, lowered, partially, full, *d*-*d* transition, Benzoic acid, benzaldehyde)

(i) The minimum amount of energy required by reactant molecules to participate in a reaction is called _______ The activation energy is _______ in presence of a positive catalyst.

(ii) Only those transition metal ions will be coloured which have _______ filled *d*-orbitals facilitating _______.

(iii) _______ will give effervescence with $NaHCO_3$ but _______ will not react.

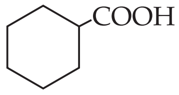
**Question 2.**

**Select and write the correct alternative from the choices given below:**

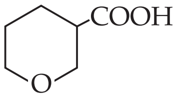
(i) The sum of co-ordination number and oxidation number of the metal M in the complex $[M(en)_2(C_2O_4)]Cl$ (where *en* is ethylenediamine) is:

(a) 6 (b) 7 (c) 8 (d) 9

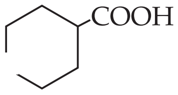
(ii) The correct order of strengths of the carboxylic acids is:



I



II



III

(a) I > II > III (b) II > III > I (c) III > II > I (d) II > I > III

(iii) Which of the following statement about primary amines is false?

- (a) Alkyl amines are stronger bases than aryl amines.
- (b) Alkyl amines react with nitrous acid to produce alcohols.
- (c) Aryl amines react with nitrous acid to produce phenols
- (d) Alkyl amines are stronger bases than ammonia.

(iv) **Assertion:** Zeolites are good shape selective catalysts.

**Reason:** Zeolites have honey comb like structure.

- (a) Both assertion and reason are true and reason is the correct explanation of assertion.
- (b) Both assertion and reason are true but reason is not the correct explanation for assertion.
- (c) Assertion is true but reason is false.
- (d) Assertion is false but reason is true.

## Section-B

**Question 3.**

(i) What is the basis of formation of the spectrochemical series?

(ii) Draw the structures of geometrical isomers of the following coordination complexes:

$$[Co(NH_3)_3Cl_3] \text{ and } [CoCl_2(en)_2]^+$$

**Question 4.**

(i) Write chemical equations to illustrate each of the following named reactions:

- (a) Stephen reaction
- (b) Perkin's reaction

**OR**

(ii) How will you bring about the following conversions? (Give equation).

- (a) Propanone to Propan-2-ol
- (b) Ethanal to 2-hydroxy propanoic acid

**Question 5.**

Write down the structures and names of the products formed when D-glucose is treated with
(i) Hydroxylamine
(ii) Acetic anhydride.

**Question 6.**

**Answer the following questions:**

(i) Ethylamine is soluble in water whereas aniline is not.

(ii) Nitro compounds have higher boiling points than the hydrocarbons having almost the same molecular mass.

**Question 7.**

What happens when D-glucose is treated with the following reagents:

(i) HI

(ii) Bromine water

**Question 8.**

A first order gas reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10h, what percentage of the initial concentration would have change in the product? What is the half-life of this reaction?

**Question 9.**

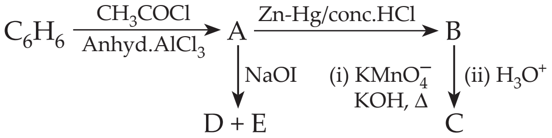
Complete and write chemical equations for the following reactions:

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine

**Question 10.**

Write the structures of A, B, C, D and E in the following reactions:



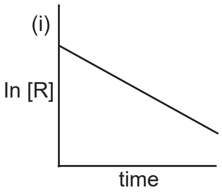
## Section-C

**Question 11.**

(i) **Answer the following questions:**

(a) An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? ($\log_{10} 2 = 0.3$)

(b) The given plot represent the variation of the concentration of a reaction R with time for reaction. What is the order of the reaction ?



**OR**

(ii) **Answer the following questions:**

The rate constant for the first order decomposition of a certain reaction is described by the equation:

$$\log k\ (s^{-1}) = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

(a) What is the energy of activation for the reaction?

(b) At what temperature will its half-life period be 256 min?

**Question 12.**

(i) Account for the following:

(a) Transition metals show variable oxidation states.

(b) $Cu^+$ ion is unstable in aqueous solution.

(ii) What is lanthanoid contraction and what is it due to? Write two consequences of lanthanoid contraction.

**Question 13.**

(i) Write the hybridization and shape of the following complexes:

(a) $[CoF_6]^{3-}$

(b) $[Ni(CN)_4]^{2-}$

(ii) What will be the correct order for the wave lengths of absorption in the visible region for the following:

$$[Ni(NO_2)_6]^{4-}, [Ni(NH_3)_6]^{2+}, [Ni(H_2O)_6]^{2+}$$

**Question 14.**

(i) Explain the forces responsible behind adsorption process of an adsorbent over in adsorbate.

(ii) What are adsorption indicators?

(iii) What is common in aqua sols and solid aerosols? How do they differ?

# Answers

## Section-A

**Answer 1.**

(i) Activation energy, lowered

**Explanation :**

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy. The activation energy is lowered in the presence of a positive catalysts because a positive catalyst increases the rate of reaction by lowering the energy of activation.

(ii) partially, *d-d* transition

**Explanation :**

Electrons can move from the lower energy *d* orbitals to the higher energy *d* orbitals by absorbing a photon of light; the wavelength of the absorbed light depends on the size of the energy gap. Any unabsorbed wavelengths of light pass through unabsorbed, and this causes the coloured appearance of the compounds.

(iii) Benzoic acid, benzaldehyde

**Explanation :**

Benzoic acid will give brisk effervescence with $NaHCO_3$ but benzaldehyde will not react. The reaction can be represented as follows:

$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + H_2O + CO_2$

$C_6H_5CHO + NaHCO_3 \rightarrow$ No reaction.

**Answer 2.**

(i) (d) 9

**Explanation :**

$[M(en)_2(C_2O_4)]Cl$

Oxidation number of metal = + 3

Coordination number of metal = 6

∴ Sum of oxidation number and coordination number = 3 + 6 = 9

Let X be the oxidation number of M

hence $X + 2(0) - 2 = +1$

$X = +3$

Thus, oxidation number is 3

Now, coordination number of M in $[M(en)_2(C_2O_4)]Cl$ is 6 because en and $C_2O_4$ are bidentate ligand.

Hence, sum of coordination number and oxidation number of M is = 6 + 3 = 9.

(ii) (b) II > III > I

**Explanation :**

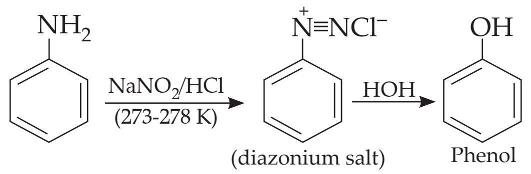
$$\text{Acidic strength} \propto -\text{I effect}$$

As oxygen is more electron withdrawing (II) and (III) show greater – I effect than (I). Thus, (I) is least acidic. Out of (II) and (III), (II) is more acidic than (III) as distance of O increases from —COOH group and acidic strength decreases.

(iii) (c) Aryl amines react with nitrous acid to produce phenols

**Explanation :**

Aryl amines react with nitrous acid to produce diazonium salts.



(iv) (a) Both assertion and reason are true and reason is the correct explanation of assertion.

**Explanation :**

The catalytic reaction that depends upon pore structure of the catalyst and the size of the reactant and product molecules is called shape selective catalysis. Hence, zeolites are microporous aluminosilicates with 3-D network of silicates in which some silicon atoms are replaced by Al-atoms giving Al-O-Si framework. Thus, zeolites are good shape selective catalysts because of their honey comb like structures. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

## Section-B

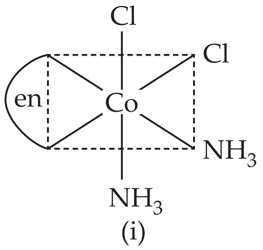
**Answer 3.**

(i) Spectrochemical series is a series in which the ligands have been arranged in order of increasing field strength.

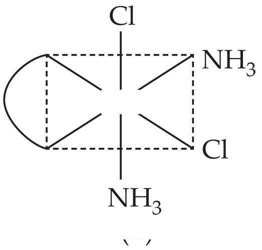
$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < Co.$$

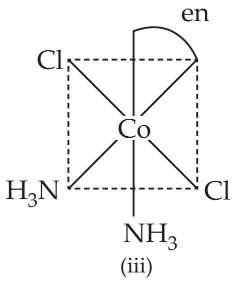
$CN^-$ is a strong field ligand and $H_2O$ is a weak field ligand hence magnitude of CFSE is different. This leads to different colour.

(ii) $[Co(NH_3)_3Cl_3]$ four geometric isomers are possible.

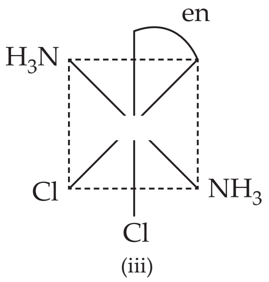


(i)





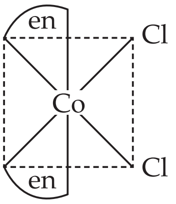
(iii)



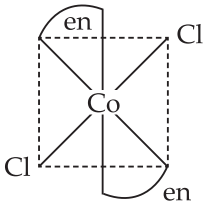
(iii)

All the four geometric isomers are un-symmetrical and each shows optical isomerism *i.e.*, forms two optical isomers *d* and *l* forms which are mirror image of each other in similar way as shown in (a).

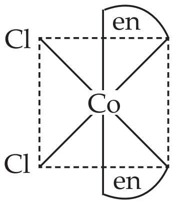
$[CoCl_2(en)_2]^+$: Two geometrical isomers cis- and transforms are possible.

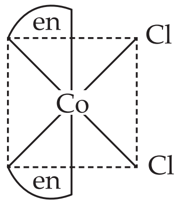


cis form
(Un-symmetrical and show optical (isomerism *d* and *l* forms are shown below)



trans form
(symmetrical and does not show optical isomerism)

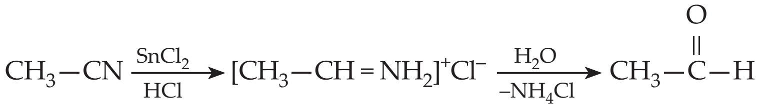




NH$_2$

**Answer 4.**

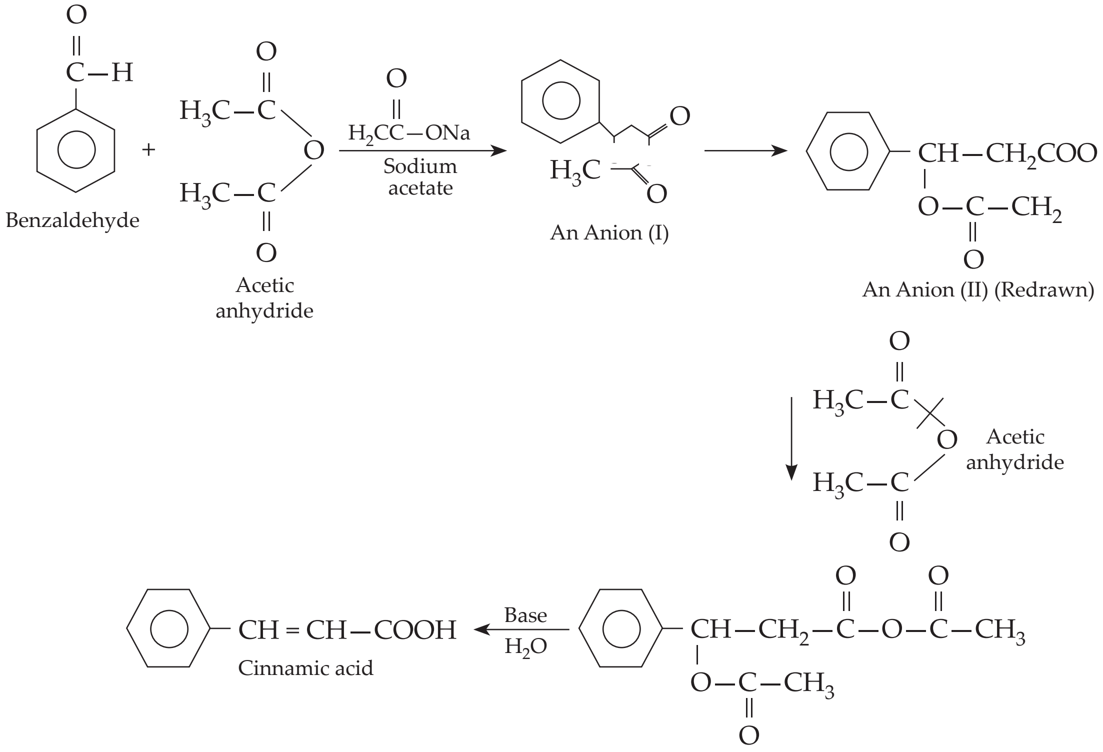
(i) (a) The Stephen reaction describes the preparation of aldehydes from nitriles with the help of tin (II) chloride and hydrochloric acid and the quenching of the resulting iminium salt with water. Another useful by product produced by this reaction is ammonium chloride. The reaction can be represented as follows:



$$CH_3-CN \xrightarrow[HCl]{SnCl_2} [CH_3-CH=NH_2]^+Cl^- \xrightarrow[-NH_4Cl]{H_2O} CH_3-\overset{\overset{O}{\|}}{C}-H$$

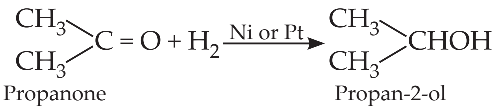
Methyl cyanide | imine intermediate | Acetaldehyde

(b) The Perkin reaction is an organic reaction developed by English chemist William Henry Perkin that is used to make cinnamic acids. It gives an $\alpha,\beta$-unsaturated aromatic acid by the aldol condensation of an aromatic aldehyde and an acid anhydride, in the presence of an alkali salt of the acid.



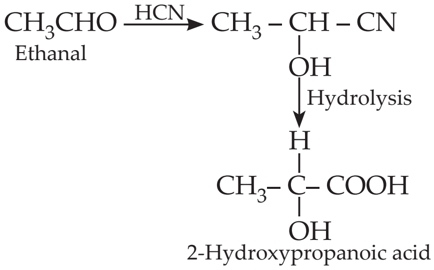
**OR**

(ii) (a)



$$\underset{\text{Propanone}}{(CH_3)_2C=O} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Propan-2-ol}}{(CH_3)_2CHOH}$$

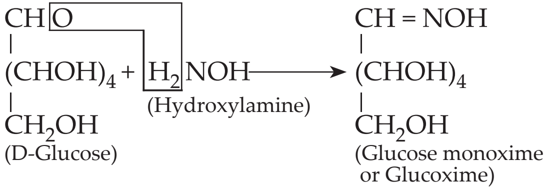
(b)



$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{HCN} CH_3-\underset{OH}{\underset{|}{CH}}-CN \xrightarrow{\text{Hydrolysis}} \underset{\text{2-Hydroxypropanoic acid}}{CH_3-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-COOH}$$

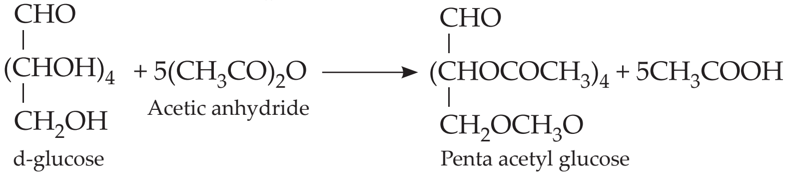
**Answer 5.**

(i) D-Glucose reacts with $H_2N-OH$ to give glucose oxime.



$$\underset{\text{(D-Glucose)}}{\begin{array}{l}CH\boxed{O}\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} + \underset{\text{(Hydroxylamine)}}{\boxed{H_2}NOH} \longrightarrow \underset{\text{(Glucose monoxime or Glucoxime)}}{\begin{array}{l}CH=NOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}$$

(ii) D-Glucose reacts with acetic anhydride to form pentacetate as a molecules of glucose contains five —OH groups. The reaction can be represented as follows:



$$\underset{\text{d-glucose}}{\begin{array}{l}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} + \underset{\text{Acetic anhydride}}{5(CH_3CO)_2O} \longrightarrow \underset{\text{Penta acetyl glucose}}{\begin{array}{l}CHO\\|\\(CHOCOCH_3)_4\\|\\CH_2OCH_3O\end{array}} + 5CH_3COOH$$

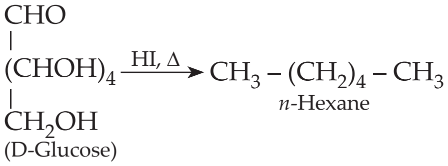
**Answer 6.**

(i) Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic bulky aryl group, the extent of hydrogen bonding decreases considerably and hence, aniline is insoluble in water.

(ii) Nitro compounds have high dipole moments and hence have strong dipole - dipole interactions. Thus, their boiling points are higher than those of hydrocarbons 'having almost the same molecular mass.

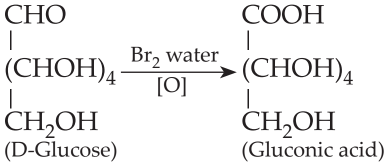
**Answer 7.**

(i) On prolonged heating with HI, D-Glucose forms n-hexane.



$$\underset{\text{(D-Glucose)}}{\begin{array}{l}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} \xrightarrow{HI,\ \Delta} \underset{n\text{-Hexane}}{CH_3-(CH_2)_4-CH_3}$$

(ii) D - Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with bromine water



$$\underset{\text{(D-Glucose)}}{\begin{array}{l}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} \xrightarrow[\text{[O]}]{Br_2\text{ water}} \underset{\text{(Gluconic acid)}}{\begin{array}{l}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}$$

**Answer 8.**

$k = 1.5 \times 10^{-6}\text{s}^{-1}$

$$kt = \text{In}\frac{100}{100-x}$$

$$\Rightarrow \qquad \text{In}\frac{100}{100-x} = 1.5 \times 10^{-6}\text{s}^{-1} \times 10 \times 60 \times 60\text{s} = 0.0054$$

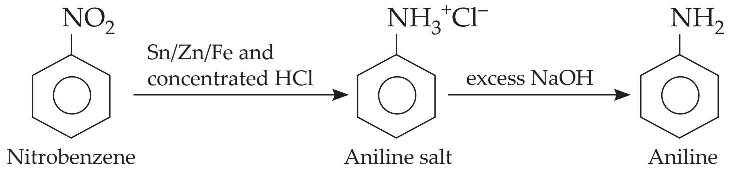
$$\Rightarrow \qquad \frac{100}{100-x} = 1.055$$

$\Rightarrow$ $x = 5.25\%$ reactant is converted into product.

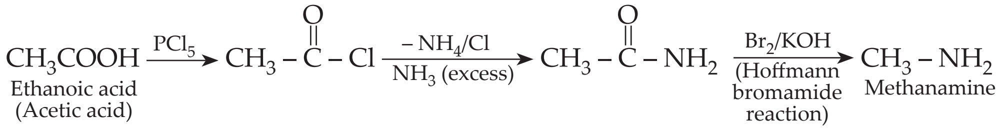
$$\text{Half-life} = \frac{\text{In}\,2}{k} = \frac{0.693}{1.5\times10^{-6}} = 462000\text{ s} = 128.33\text{ h}$$

**Answer 9.**

(i)

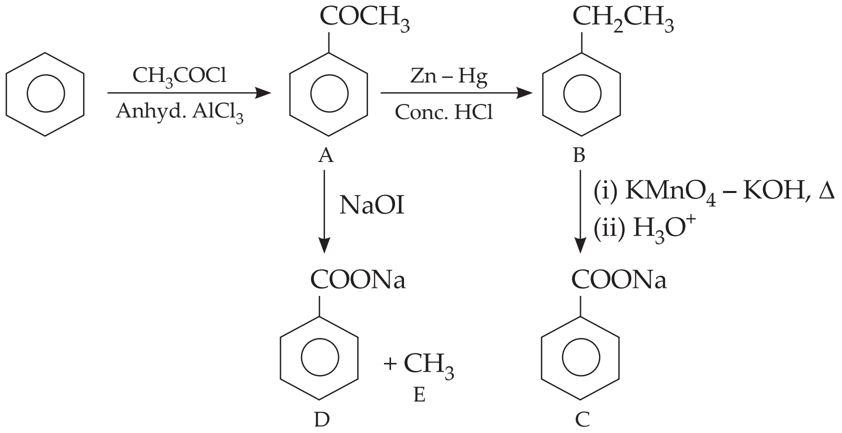


(ii)



$$\underset{\substack{\text{Ethanoic acid}\\\text{(Acetic acid)}}}{CH_3COOH} \xrightarrow{PCl_5} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[NH_3\text{ (excess)}]{-NH_4/Cl} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\substack{\text{(Hoffmann}\\\text{bromamide}\\\text{reaction)}}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3-NH_2}$$

**Answer 10.**



## Section-C

**Answer 11.**

(i) (a) For a first order process $K_t = ln\ \frac{[A_0]}{[A]}$

where $[A_0]$ = initial concentration

[A] = concentration of reactant remaining at time $t$

$$\Rightarrow \qquad K_{t_{1/8}} = ln\frac{[A_0]}{[A_0]/8} = ln\ 8 = 2.303\ (\log_{10} 2) \times 3 \qquad ...(i)$$

$(\because ln\ x = 2.303 \log_{10} x)$

$$\text{and} \qquad K_{t_{1/10}} = ln\frac{[A_0]}{[A_0]/10} = ln 10 = 2.303\ (\log_{10} 10) \qquad ...(ii)$$

As we know log 10 = 1

(now on comparing both equation (i) and (ii), we get)

$$\frac{K_{t_{1/8}}}{K_{t_{1/10}}} = \frac{2.303 \times 0.3 \times 3}{2.303}$$

$$\frac{t_{1/8}}{t_{1/10}} = 0.3 \times 3$$

Thus,

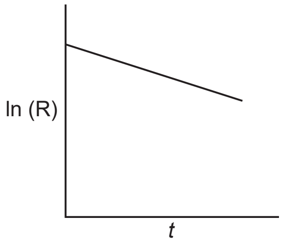
$$\therefore \qquad \frac{t_{1/8}}{t_{1/10}} \times 10 = 0.3 \times 3 \times 10 = 9$$

(b) First order reaction:

Because in first order reaction, the rate expression depends on the concentration of one species only having power equal to unity.

$$nR \rightarrow \text{products}$$

$$\frac{-d[R]}{dt} = k[R]$$



On integration, $-\ln[R] = kt - \ln[R_0]$

$$\text{or} \qquad \ln(R) = \ln(R_0) - kt$$

$$y = c + mx$$

$$m = \text{slope} = -k \text{ (negative)}$$

$$c = \text{intercept} = \ln(r_0)$$

The graph is for first order reactions.

**OR**

(ii) (a) The Arrhenius equation is:

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

(where log A = 14.34)

Comparing with the given equation:

$$1.25 \times 10^4 = \frac{E_a}{2.303\,R} \Rightarrow E_a = 239.33\,\text{kJ mol}^{-1}$$

$(R = 8.31 \times 10^{-3}$ kJ/mol.K)

(b) When half-life = 256 min,

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{256 \times 60}\,s^{-1} = 4.5 \times 10^{-5}\,s^{-1} \qquad \left(\because k = \frac{0.693}{t_{1/2}}\right)$$

$$\Rightarrow \qquad \frac{1.25\times10^4}{T} = 14.34 - \log 4.5 \times 10^{-5} = 18.686 \qquad (\because \log 4.5 \times 10^{-5} = -4.346)$$

$$\Rightarrow \qquad T = \frac{1.25\times10^4}{18.686} = 669 \text{ K}$$

**Answer 12.**

(i) (a) Transition elements show variable oxidation states because their valence electrons are in two different sets of orbitals, that is (n – 1)*d* and *ns*. The energy difference between these orbitals is very less, so both the energy levels can be used for bond formation. Thus, transition elements have variable oxidation states.

For example: Sc has $ns^2\ (n-1)d^1$ electronic configuration.

If it utilizes two electrons from its *ns* subshell then its oxidation state is +2. When it utilizes electrons from both the subshell *i.e.*, *ns* and (*n* – 1)*d* then its oxidation state is +3.

(b) In aqueous solutions, $Cu^+$ undergoes disproportionation to form a more stable $Cu^{2+}$ ion.

$$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

$Cu^{2+}$ in aqueous solutions in more stable than $Cu^+$ ion because hydration enthalpy of $Cu^{2+}$ is higher than that of $Cu^+$. It compensates the second ionisation enthalpy of Cu involved in the formation of $Cu^{2+}$ ions.

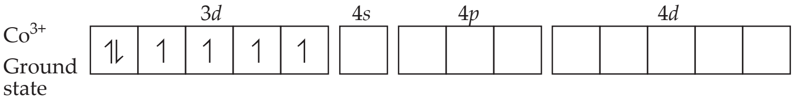
(ii) The atomic size or ionic radii of tripositive lanthanide ions decreases steadily from La to Lu due to increasing nuclear charge and electrons entering the inner (*n*–2) *f* orbital. This gradual decrease in the size with an increasing atomic number is called lanthanide contraction.

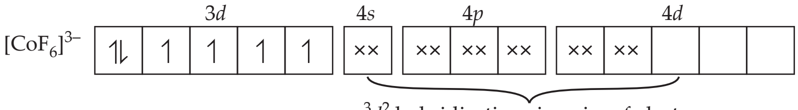
**Consequences of Lanthanide Contraction:**

1. The size of the atom of the third transition series is closely the same as that of the atom of the second transition series.
2. Due to smaller size but higher nuclear charge, they have tendency to form coordinate and undergo complex formation.

**Answer 13.**

(i) (a) Oxidation state of Co ion in $[CoF_6]^{3-}$ is + 3.



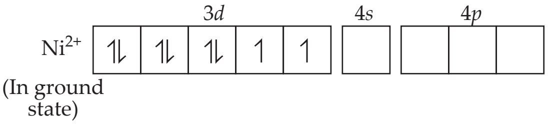


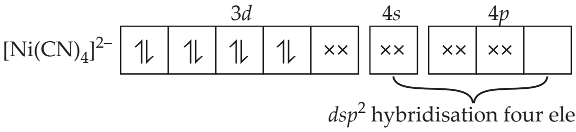
$sp^3d^2$ hybridisation six pairs of electrons from six $F^-$ ion (Weak ligands)

**Structure -** Outer orbital octahedral complex.

**Nature -** Paramagnetic

(b) In $[Ni(CN)_4]^{2-}$ : Ni is present as Ni(II) with $3d^8$ configuration





$dsp^2$ hybridisation four electron pairs donated by four $CN^-$ ions. (Strong ligand)

The complex ion has square planar geometry and is diamagnetic in nature.

(ii) All the complex ions are derived from $Ni^{2+}$ ion with different ligands. From the position of the ligands in the spectrochemical series the order of ligand field strength is:

$$H_2O < NH_3 < NO_2$$

That means $\Delta_0$ for $NO_2^-$ is maximum and so it would adsorb the radiation of shorter wavelength having high energy. So, the order of absorption of the wavelength in the visible region is:

$$\underset{(\lambda \text{ about } 700 \text{ nm})}{[Ni(H_2O)_6]^{2+}} > \underset{(\text{about } 500 \text{ nm})}{[Ni(NH_3)_6]^{2+}} > \underset{(< 500 \text{ nm})}{[Ni(NO_2)_6]^{4-}}$$

**Answer 14.**

(i) Adsorption occur when the surface particles of adsorbent experience the unbalanced attractive forces from the bulk, but on the surface the particles are not surrounded by atoms or molecules from all side. These unbalanced attractive forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.

(ii) Adsorption indicators are substances that indicate an excess of a reactant in argentometric titrations. Precipitate becomes coloured when adsorption indicators are adsorbed. In such titrations, dyestuffs like eosin, fluorescein, alizarin red etc. are used as adsorption indicators.

(iii) Aquasol and solid aerosol both have solid as the dispersed phase. They differ in dispersion medium. Aquasols have water as the dispersion medium while aerosols have gas as the dispersion medium.

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