# Class XII Session 2023-24 Subject - Chemistry Sample Question Paper - 4

Time Allowed: 3 hours Maximum Marks: 70

#### **General Instructions:**

Read the following instructions carefully.

- 1. There are **33** questions in this question paper with internal choice.
- 2. SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
- 3. SECTION B consists of 5 very short answer questions carrying 2 marks each.
- 4. SECTION C consists of 7 short answer questions carrying 3 marks each.
- 5. SECTION D consists of 2 case-based questions carrying 4 marks each.
- 6. SECTION E consists of 3 long answer questions carrying 5 marks each.
- 7. All questions are compulsory.
- 8. Use of log tables and calculators is not allowed.

#### Section A

Decomposition of benzene diozonium chloride by using Cu<sub>2</sub>Cl<sub>2</sub>/HCl to form chlorobenzene is: [1] 1. a) Wurtz – Fittig reaction b) Friedel – Crafts reaction c) Sandmeyer's reaction d) Finkelstein reaction 2. DNA fingerprinting means the [1] a) sequencing the nucleotides in DNA b) sequencing the bases present in double helix c) information regarding the unique sequence d) information reagrding the unique imprints of bases on DNA for a person on the fingertip for a person 3. [1] Which of the following reagents can be used to oxidise primary alcohols to aldehydes? a) All of these b) CrO<sub>3</sub> in an anhydrous medium. c) Heat in the presence of Cu at 573K. d) Pyridinium chlorochromate. The compound formed as a result of oxidation of ethyl benzene by  $KMnO_4$  is [1] 4. a) Benzophenone b) Acetophenone c) Benzoic acid d) Benzyl alcohol 5. The metabolism of hormones in human body is an example of [1] b) First order reaction a) Second order reaction c) Pseudo first order reaction d) Pseudo second order reaction 6. [1] Match the items given in column I with that in column II:

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Column I	Column II
(a) Osmotic Pressure.	(i) Cottrell's method.
(b) Relative lowering of vapour pressure.	(ii) Rast's method.
(c) Elevation in boiling point.	(iii) Ostwald and Walker's method.
(d) Depression in freezing point.	(iv) Berkeley and Hartley's method.

- a) (a) (iv), (b) (iii), (c) (i), (d) (ii).
- b) (a) (iv), (b) (iii), (c) (ii), (d) (i).
- c) (a) (i), (b) (ii), (c) (iii), (d) (iv).
- d) (a) (i), (b) (iv), (c) (ii), (d) (iii).
- 7. Which reagent will you use for the following reaction?

[1]

 $CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$ 

- a)  $\text{Cl}_2$  gas in the presence of iron in dark
- b) NaCl + H<sub>2</sub>SO<sub>4</sub>

c) Cl<sub>2</sub> gas in dark

- d) Cl<sub>2</sub>/UV light
- 8. The catalyst used in Deacon's process is:

[1]

a) Cu<sub>2</sub>Cl<sub>2</sub>

b) FeCl<sub>2</sub>

c) FeCl<sub>3</sub>

- d) CuCl<sub>2</sub>
- 9. If the reaction 2 A + 3 D  $\rightarrow$  product is first order in A and second order in D, then the rate law will have the form: rate =

[1]

a)  $k[A][D]^2$ 

b) K [A] [D]

c)  $K[A]^2[D]^2$ 

- d)  $K[A]^{2}[D]$
- 10. When ethanal is heated with Fehlings solution, it gives a precipitate of:

[1]

a)  $Cu + Cu_2O + CuO$ 

b) CuO

c) Cu

- d) Cu<sub>2</sub>O
- 11. Give IUPAC name of the compound given below.

[1]

- a) 2 Chloro 5 hydroxyhexane
- b) 5 Chlorohexan 2 ol
- c) 2 Hydroxy 5 chlorohexane
- d) 2 Chlorohexan 5 ol
- 12. Which of the following compounds is the weakest Brönsted base?

[1]

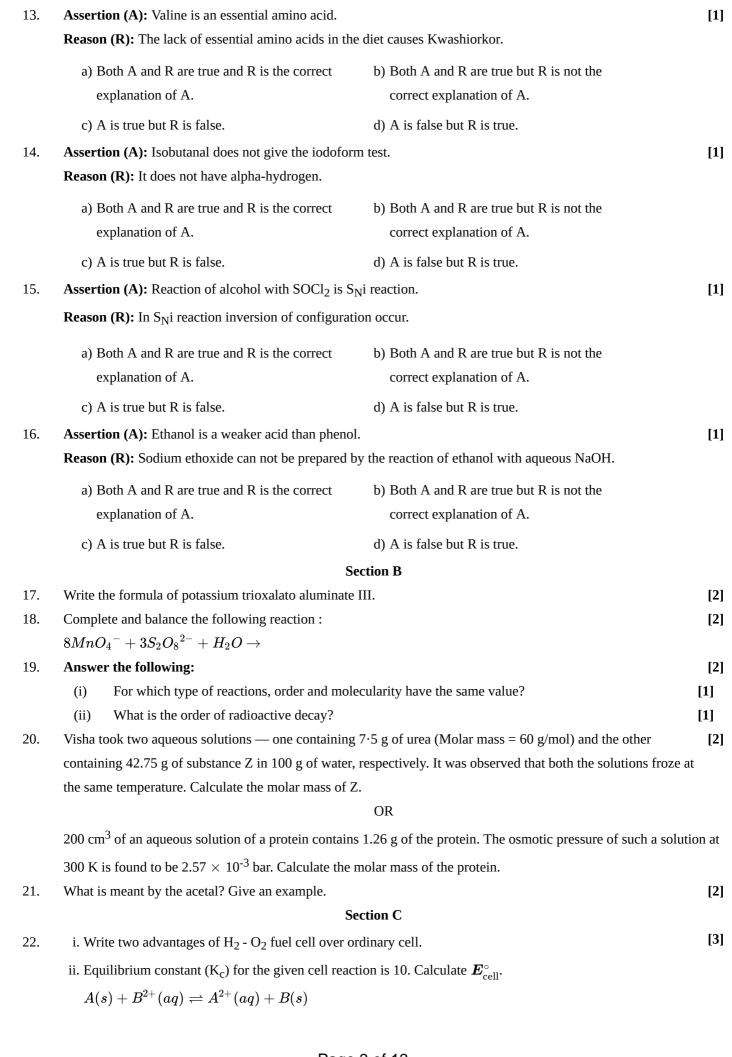




c) NH



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23. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will [3] be completed.

Given:  $\log 2 = 0.3010$ ,  $\log 3 = 0.4771$ ,

log 4 = 0.6021

Why is the reactivity of all the three classes of alcohols with conc. HCl and ZnCl<sub>2</sub> (Lucas reagent) different? [3] 24.

OR

Give the major products that are formed by heating each of the following ethers with HI.

i. 
$$CH_3-CH_2-\overset{CH_3}{CH}-CH_2-O-CH_2-CH_3$$
 ii.  $CH_3-CH_2-CH_2-O-\overset{CH_3}{\overset{C}{C}}-CH_2-CH_3$ 

25. Explain the mechanism of nucleophilic addition to a carbonyl group and give one example of such addition reactions.

26. Calculate the emf of the following cell at 25°C. [3]

[3]

$$Ag\left(s\right)\mid Ag^{+}\!(10^{\text{-}3}\,\text{M})\parallel \text{Cu}^{2+}\!(10^{\text{-}1}\,\text{M})\mid \text{Cu}\left(s\right)$$

[Given,
$$E^{o}_{cell}$$
 = +0.46 V and log 10<sup>n</sup> = n]

27. How will you effect the following conversions? [3]

i. Chlorobenzene to p-nitrophenoI.

ii. Bromobenzene to biphenyl.

iii. Propene to propan-1-ol

28. Write the Nernst equation and calculate emf of the following cell at 298 K:

 $Cr \mid Cr^{3+} (0.1 \text{ M}) \parallel Fe^{2+} (0.01 \text{ M}) \mid Fe$ 

Given : 
$$E_{\mathrm{Cr}^{3+}/\mathrm{Cr}}^{\ominus}$$
 = -0.75 V

$$E_{Fe^{2+}/Fe}^{\ominus} = -0.45 \text{ V}$$

 $(\log 10 = 1)$ 

**Section D** 

29. Read the text carefully and answer the questions: [4]

[3]

The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is  $(n - 1)d^{1-10} ns^{1-2}$ . The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e. 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation stables, complex formation, formation of coloured ions, alloys, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

(i) Why are Zn, Cd and Hg non-transition elements?

Why are melting points of transition metals high?

Which transition metal of 3d series does not show variable oxidation state? (ii)

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(iii) Why do transition metals and their compounds show catalytic activity?

## 30. Read the text carefully and answer the questions:

[4]

The solutions which boil at a constant temperature like a pure liquid and possess the same composition in liquid, as well as vapour state are called azeotropes. The components of azeotropes cannot be separated by fractional distillation. Only non-ideal solutions form azeotropes. Solutions with negative deviation form maximum boiling azeotrope and the solutions with positive deviation form minimum boiling azeotrope. The boiling point of azeotrope is never equal to the boiling points of any of the components of the azeotrope.

- (i) The azeotropic solutions of two miscible liquids show what type of deviation from Raoult's law?
- (ii) The azeotropic mixture of water & HCI boils at  $108.5^{\circ}C$ . What type of deviation is shown by the solution? Does this solution behave as ideal or non-ideal?
- (iii) Do ideal solutions form azeotropes?

OR

Out of pure liquid and azeotrope showing positive deviation, Which one has a higher boiling point?

#### **Section E**

31. Attempt any five of the following:

- [5] [1]
- (i) How do you explain the presence of all six carbon atoms in glucose in a straight chain?

[1]

(ii) What is the structural feature characterising reducing sugars?

[1]

(iii) Write the name of the component of starch which is water-soluble.

[1]

(iv) What is the difference between a glycosidic linkage and a peptide linkage?(v) Define native state in reference to proteins.

[1]

(vi) Name the linkage connecting monosaccharide units in polysaccharides.

[1]

(vii) Which vitamin is linked with anti-sterility?

[1]

32. Explain with two examples each of the following: Coordination entity, ligand coordination number, coordination [5] polyhedron, homoleptic and heteroleptic.

OR

Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

33. i. Write the structures of main products when benzene diazonium chloride reacts with the following reagents:

[5]

- a.  $H_3PO_2 + Hp$
- b. CuCN/KCN
- c. H<sub>2</sub>O
- ii. Arrange the following in the increasing order of their basic character in an aqueous solution:  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $(C_2H_5)_3N$ . Give justification.

OR

Account for the following:

- i. Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- ii. Amines are more basic than alcohols of comparable molecular masses.

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## **Solution**

## **Section A**

1.

(c) Sandmeyer's reaction

Explanation:  $C_6H_5N_2^+Cl^-+Cu_2Cl_2/HCl o C_6H_5Cl$ 

Mixing the solution of the freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br. This is called Sandmeyer's reaction.

2.

(c) information regarding the unique sequence of bases on DNA for a person

**Explanation:** A sequence of bases on DNA is unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment.

3. **(a)** All of these

**Explanation: Oxidation of alcohols to aldehydes is partial oxidation**; aldehydes are further oxidized to carboxylic acids. Conditions required for making aldehydes are heat and distillation.

In aldehyde formation, the temperature of the reaction should be kept above the boiling point of the aldehyde and below the boiling point of the alcohol.

These include:

- Chromium-based reagents, such as Collins reagent (CrO<sub>3</sub>·Py<sub>2</sub>)
- PDC or PCC.
- Heat in the presence of Cu at 573K.

4.

(c) Benzoic acid

#### **Explanation:**

Alkylbenzenes having at least one alpha hydrogen when reacts with KMnO<sub>4</sub> then, alkyl group oxidises to COOH group.

5.

(c) Pseudo first order reaction

**Explanation:** It is a pseudo-first-order reaction. Pseudo means false. It appears to be a second-order reaction but actually, it is a first-order reaction.

6. **(a)** (a) - (iv), (b) - (iii), (c) - (i), (d) - (ii).

**Explanation:** (a) - (iv), (b) - (iii), (c) - (i), (d) - (ii).

7.

(d) Cl<sub>2</sub>/UV light

Explanation: Production of alkyl chlorides from alkanes can be carried out by chlorination under the presence of UV light.

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Chlorine molecule( $Cl_2$ ) under the influence of UV light forms free radicals, which react with alkanes to form a mixture of isomeric monohaloalkane and polyhaloalkanes.

8.

(d) CuCl<sub>2</sub>

**Explanation:** CuCl<sub>2</sub> is used as a catalyst in Deacon's Process.

9. **(a)**  $k[A][D]^2$ 

**Explanation:** Rate of reaction is first-order w.r.t A reactant and 2<sup>nd</sup>-order w.r.t D reactant, therefore:

$$rate = k[A][D]^2$$

10.

(d) Cu<sub>2</sub>O

aldehydes give positive fehling's test with a red precipitate of Cu<sub>2</sub>O

11.

**(b)** 5 - Chlorohexan - 2 - ol

Explanation: 
$$CH_3$$
  $\overset{6}{\overset{}{\overset{}{C}}}H - CH_2 - CH_2 - \overset{3}{\overset{}{\overset{}{C}}}H - \overset{1}{\overset{}{\overset{}{\overset{}{C}}}H - \overset{1}{\overset{}{\overset{}{C}}}H_2}$ 

-OH is given preference over -Cl so numbering is done so that -OH gets the lowest number.

12.

**Explanation:** 



is weakest Brönsted base.

13.

**(b)** Both A and R are true but R is not the correct explanation of A.

**Explanation:** Valine is an essential amino acid. The amino acids which the body cannot synthesize are called an essential amino acid.

14.

**(c)** A is true but R is false.

**Explanation:** Isobutanal does not give an iodoform test because it does not have the -COCH<sub>3</sub> group.

15.

**(c)** A is true but R is false.

**Explanation:** A is true but R is false.

16.

**(b)** Both A and R are true but R is not the correct explanation of A.

**Explanation:** Phenol is a stronger acid than ethanol as phenoxide ion is stabilized by resonance whereas no such stabilization occurs in ethoxide ion.

Sodium ethoxide can be prepared by the reaction of ethanol with sodium.

Section B

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17. K<sub>3</sub>[Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>

18. In neutral and slight alkaline medium  $MnO_4^-$  will reduce to  $MnO_2$  and thiosulphate is oxidised almost quantitatively to sulphate.

$$8Mn{O_4}^- + 3{S_2}{O_3}^{2-} + H_2O \rightarrow 8Mn{O_2} + 6S{O_4}^{2-} + 2OH^-$$

- 19. Answer the following:
  - (i) Elementary reactions have the same value of order and molecularity because the elementary reaction proceeds in a single step.
  - (ii) First order.

20. 
$$\triangle T_f$$
 = molality  $\times$  K<sub>f</sub>

Since  $\triangle T_f$  is same for both solutions,

i.e. 
$$riangle T_{f_1} - \Delta T_{f_2}$$
 (given)

$$molality_{(urea)} \times K_f = molality_{(x)} \times K_f$$

$$\frac{\frac{7}{60} \times 1000}{100} = \frac{\frac{42}{M_{w(x)}} \times 1000}{100}$$
 $M_{w} = \frac{42 \times 60}{7} = 360 \text{ gm}$ 

Hence, molar mass of Z = 360gm.

OR

The various quantities known to us are as follows osmotic pressure of solution  $\Pi$  = 2.57  $\times$  10<sup>-3</sup> bar.

$$V = 200 \text{ cm}^3 = 0.200 \text{ litre}$$

$$T = 300 \text{ K}$$

$$R = 0.083 L bar mol^{-1} K^{-1}$$

Substituting these values in equation (2.42) we get

$$M_2 = \frac{^{1.26 g \times 0.083 LbarK^{-1} mol^{-1} \times 300 K}}{^{2.57 \times 10^{-3} bar \times 0.200 L}} = 61.022 \ g \ mol^{-1}$$

21. Gem-dialkoxy alkanes in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in presence of dry HCl gas.

$$CH_3 \longrightarrow C = O + \underbrace{H \longrightarrow OCH_2CH_3}_{Acetaldehyde} \underbrace{Dry \ HCl \ gas, \Delta}_{Dry \ HCl \ gas, \Delta} \underbrace{CH_3}_{H} \longrightarrow C \underbrace{OCH_2CH_3}_{OCH_2CH_3} + H_2O$$
Acetaldehyde

Ethyl alcohol

Acetaldehyde diethyl acetal

These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehyde group in organic synthesis.

### **Section C**

- 22. i. Advantages of fuel cells:
  - a. Fuel cells are highly efficient. These cells produce electricity with an efficiency of about 70% compared to the thermal plants whose efficiency is about 40%.
  - b. Because of the continuous supply of fuels, these cells never become dead. These cells are usually operated at a temperature of  $70-140^{\circ}$ C and give a potential of about 0.9V.
  - c. Fuel cells do not cause any pollution, unlike thermal plant which burns fossil fuels like coal gas, oil, etc.
  - ii. The reaction

$$A(s)+B^{2+}(aq) 
ightleftharpoons A^{2+}(aq)+B(s)$$

By using the Nernst equation

$$E_{
m cell}$$
 =  $E_{
m cell}^{\circ}$  -  $rac{0.059}{n} {
m log} rac{\left[A^{2+}
ight]}{\left[B^{2+}
ight]}$ 

At equilibrium,  $E_{\rm cell}$  = 0,

$$E_{
m cell}^\circ$$
 =  $rac{0.059}{n}$ log  $K_C$ 

$$K_c = 10$$
 and  $n = 2$  (Given)

$$E_{
m cell}^{\circ} = rac{0.059}{2} {
m log} \, 10$$
  $E_{
m cell}^{\circ} = rac{0.059}{2} = 0.0295$ 

23. For a fiirst order reaction,  $k = \frac{2.303}{t} \log \frac{a}{a-x}$ 

where, k = Rate constant

a = Initial concentration

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(a - x) =concentration after time 't',

When a first order reaction is 25% completed in 20 min.

$$a = 100$$
,  $a - x = 100 - 25 = 75$ ,  $t = 20$  min.

$$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{20} \log \frac{100}{75}$$

$$= \frac{2.303}{20} [\log 4 - \log 3] = 0.0143 \,\mathrm{min}^{-1}$$

For 75% completion of reaction.

$$a = 100$$
,  $a - x = 100 - 75 = 25$ ,  $k = 0.0143 \text{ min}^{-1}$ 

For 75% completion of reaction.

$$a = 100$$
,  $a - x = 100 - 75 = 25$ ,  $k = 0.0143 \text{ min}^{-1}$ 

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2303}{0.0143} \log \frac{100}{25}$$
$$= \frac{2.303}{0.0143} \log 4 = 96.968$$

$$=\frac{2.303}{0.0143}\log 4 = 96.968$$

24. The alcohol combines with HCl to form protonated alcohol. The positive charge on oxygen weakens the C - O bond leading to its cleavage.

a. 
$$R - \ddot{O} - H + HCI \stackrel{fast}{\rightleftharpoons} R - \ddot{O} - H + CI^-$$

b. 
$$R \leftarrow O - H \xrightarrow{slow} R^{+} + H_2O$$

$$c.\ R^+ + Cl^- \stackrel{fast}{\longrightarrow} RCl$$

The rate-determining step in the above mechanism is (b), which is a slow step reaction. The stability of carbocation will determine the reactivity of the reaction. since the order of stability of carbocation is primary. < secondary. < tertiary. Higher the stability of carbonium ion faster the reaction of the alcohol with the nucleophile Cl<sup>-</sup>. Hence the order of formation of an alkyl halide in the above reaction is primary < secondary < tertiary.

i. 
$$CH_3-CH_2-CH-CH_2OH+CH_3CH_2I$$
  $CH_3$   $CH_3$   $CH_2$   $CH_2$ 

ii. 
$$CH_3CH_2CH_2OH+CH_3CH_2-egin{pmatrix} CH_3 & & CH_3 & & \\ & & & & CH_3CH_2-CH_3 & & \\ & & & & CH_3 & & \\ & & & & CH_3 & & \\ & & & CH_3 &$$

iii.

$$\bigcirc$$
 CH<sub>2</sub>I +  $\bigcirc$  OH

25. Step I: A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp<sup>2</sup> hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp<sup>2</sup> to sp<sup>3</sup> in this process and a tetrahedral alkoxide intermediate is produced.

$$\overline{Nu}$$
: +  $C = 0$ :  $C - \overline{0}$ :

**Step II:** This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu<sup>-</sup> and H<sup>+</sup> across the carbon-oxygen double bond is shown in the figure.

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An example is given below:

$$CH_3 - C - H + HCN 
ightarrow CH_3 - C - H$$
 $Acetaldehyde$ 
 $Acetaldehyde$ 
 $Cyanohydrin$ 

26. The given cell is , Ag (s)  $|Ag^{+}(10^{-3}M)| Cu^{2+}(10^{-1}M) | Cu(s)$ 

**At anode** 
$$Ag(s) \rightarrow Ag^{+}(aq) + e^{-}] \times 2$$

**At cathode,** 
$$Cu^{2+} + 2e^{-} \rightarrow Cu$$
 (s)

Overall reaction; 
$$2Ag(s) + Cu^{2+}(aq) \rightarrow 2Ag^{+} + Cu(s)$$

Now, applying Nernst equation, 
$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.0591}{2} \log \frac{[Ag^{2+}]}{[Cu^{2+}]} = 0.46 - \frac{0.0591}{2} \log \frac{(10^{-3})^2}{10^{-1}} = 0.46 - \frac{0.0591}{2} \log 10^{-5}$$

Therefore,  $E_{cell} = 0.608 \text{ V}$ 

#### 27. Steps involved in the following conversions are as under:

#### Section D

#### 29. Read the text carefully and answer the questions:

The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is  $(n - 1)d^{1-10} ns^{1-2}$ . The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e. 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation stables, complex formation, formation of coloured ions, alloys, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

(i) It is because neither they nor their ions have incompletely filled d-orbitals.

OF

It is due to strong interatomic forces of attraction due to presence of unpaired electrons.

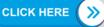
- (ii) Scandium (Sc) and Zinc (Zn).
- (iii)It is because they show variable oxidation state, can form intermediate complexes and have large surface area for adsorption of gases.

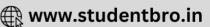
#### 30. Read the text carefully and answer the questions:

The solutions which boil at a constant temperature like a pure liquid and possess the same composition in liquid, as well as vapour state are called azeotropes. The components of azeotropes cannot be separated by fractional distillation. Only non-ideal solutions

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form azeotropes. Solutions with negative deviation form maximum boiling azeotrope and the solutions with positive deviation form minimum boiling azeotrope. The boiling point of azeotrope is never equal to the boiling points of any of the components of the azeotrope.

- (i) The azeotropic solutions of two miscible liquids may show positive or negative deviation from Raoult's law.
- (ii) The solution is a non-ideal solution and shows a negative deviation from Raoult's law.
- (iii)No, ideal solutions don't form azeotropes. Only the non-ideal solution form azeotrope.

OR

The boiling point of a pure liquid is higher as compared to azeotrope showing positive deviation.

#### Section E

- 31. Attempt any five of the following:
  - (i) Glucose on prolonged heating with HI and red phosphorus gives n-hexane HI (excess) suggest that all six carbon atom are in straight chain.

$$\substack{C_6H_{12}O_6\frac{H1(excess)}{\Delta}CH_3CH_2CH_2CH_2CH_2CH_3\\ n-Hexane\ (straight\ chain)}$$

- (ii) The reducing sugars have free aldehydic or ketonic groups.
- (iii)The component of starch which is water-soluble Amylose.
- (iv)**Glycosidic linkage:** It is the linkage which joins two monosaccharides through oxygen atom. It is present in carbohydrates.

Peptide Linkage: It is the linkage which joins two amino acids through - CO-NH- bond. It is present in proteins.

- (v) Native state of protein is the sequence in which the amino acids are linked together with the help of peptide bond.
- (vi)The monosaccharide units are linked through the glycosidic linkage in the polysaccharide.
- (vii)Vitamin E.
- 32. **Coordination** entity: This entity usually constitutes a central metal atom or ion, to which are attached a fixed number of other atoms or ions or groups by coordinate bonds. Examples are [Ni(CO)<sub>4</sub>], [COCl<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>], etc.

**Ligands:** It is an ion having at least one lone pair of electrons and capable of forming a coordinate bond with central atom / ion in the coordination entity.

Examples are : Cl<sup>-</sup>, (OH)<sup>-</sup>, (CN)<sup>-</sup>etc.

**Coordinate number:** The total number of coordinate bonds with which central atom/ ion is linked to ligands in the coordination entity is called coordination number of central atom / ion.

Coordination polyhedron: The spatial arrangement of the ligands which are directly attached to the central atom / ion defines a coordination polyhedron about the central atom.

Examples are:  $[Co(NH_3)_6]^{3+}$  is octahedral,

[Ni(CO)<sub>4</sub>]is tetrahedral.

Homoleptic and hedroleptic: Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic.

Example  $[CO(NH_3)_6]^{3+}$ 

Complex in which a metal is bound to more than one kind of donor groups are called hetroleptic. Example: [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>

OR

i. Coordination entity: A coordination entity is an electrically charged radical or species carrying a positive or negative charge. In a coordination entity, the central atom or ion is surrounded by a suitable number of neutral molecules or negative ions (called ligands). For example:

$$[Ni(NH_3)_6]^{2+}$$
,  $[Fe(CN)_6]^{4+}$  =cationic complex

$$[PtCl_4]^{2-}$$
,  $[Ag(CN)_2]^-$  = anionic complex

$$[Ni(CO)_4]$$
,  $[Co(NH_3)_4Cl_2]$  = neutral complex

ii. Ligands

The neutral molecules or negatively charged ions that surround the metal atom in a coordination entity or a coordinal complex are known as ligands. For example,NH<sub>3</sub>,H<sub>2</sub>O,Cl<sup>-</sup>and OH<sup>-</sup>. Ligands are usually polar in nature and possess at least one unshared pair of valence electrons.

iii. Coordination number:

The total number of ligands (either neutral molecules or negative ions) that get attached to the central metal atom in the

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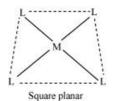


coordination sphere is called the coordination number of the central metal atom. It is also referred to as its ligancy. For example:, there as six chloride ions attached to Pt in the coordinate sphere. Therefore, the coordination number of Pt is 6.

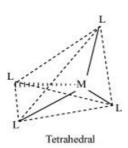
- a. In the complex, $K_2[PtCl_6]$
- b. Similarly, in the complex [Ni(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>,the coordination number of the central atom (Ni) is 4.
- iv. Coordination polyhedron:

Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere. For example:

a.



b.



- v. Homoleptic complexes: These are those complexes in which the metal ion is bound to only one kind of a donor group. For eg:  $[Co(NH_3)_6]^{3+}$ ,  $[PtCl_4]^{2-}$ , etc.
- vi. Heteroleptic complexes: Heteroleptic complexes are those complexes where the central metal ion is bound to more than one type of a donor group.

For e.g.: $[Co(NH_3)_4Cl_2]^+$ ,  $[Co(NH_3)_5Cl]^{2+}$ 

ii. The relative basic strength of  $C_2H_5NH_2$ ,  $(C_2H5)_2NH$  and  $(C_2H_5)_3N$  depends upon the stabilisation of their corresponding conjugate acids (formed as a result of accepting a proton from water by a number of factors such a; B-bonding, steric hindrance of the alkyl groups and +I-effect of the alkyl groups. All these factors are favourable for  $2^0$  amines, therefore,  $((C_2H5)_2NH)$  is a stronger base than  $C_2H_5NH_2$  and  $((C_2H_5)_3N)$ . Since,  $C_2H_5$  group is large, it exerts some steric hindrance to H-bond.

Therefore, stabilisation of the conjugate acid derived from  $(C_2H_5)_3N$  is due to mainly by +I-effect which is greater than the stabilisation of the conjugate acid derived from  $C_2H_5NH_2$  by H-bonding.

$$\begin{array}{c} H_5C_2 \\ H_5C_2 \end{array} N \begin{array}{c} H \\ \text{is more stable than} \\ H_5C_2 - N \end{array} \stackrel{\stackrel{\delta_+}{\leftarrow}}{\underset{\stackrel{\delta_-}{\leftarrow}}{\overset{\delta_-}{\leftarrow}}} \cdots \stackrel{\stackrel{\delta_-}{\rightarrow}}{\underset{\stackrel{\delta_-}{\leftarrow}}{\overset{\delta_-}{\leftarrow}}} \cdots \stackrel{\delta_-}{\rightarrow} \\ H \cdots OH_2 \\ \stackrel{\delta_+}{\leftarrow} \cdots OH_2 \\ \stackrel{\delta_+}{$$

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Thus,  $(C_2H_5)_3N$  is more basic than  $C_2H_5NH_2$ . Hence, the overall basic strength of the three amines increases in the order:  $C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$ .

OR

i. The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring as shown below.

- ii. Amines are more basic than alcohols of comparable masses because
  - a. N-atom being less electronegative can easily donate its lone pair of electrons to a proton than more electronegative 0-atom which hold electrons more tightly than N. Hence, amines are more basic than alcohols.
  - b. When an amine accepts a proton, the ammonium salt is formed and when alcohol accepts a proton oxonium salt is formed.

$$R$$
— $\stackrel{\circ}{N}$  $H_2$  +  $H^+$  — $\stackrel{\circ}{M}$  $R$ — $\stackrel{\circ}{N}$  $H_3$   
Ammonium salt (More stable)  
 $R$ — $\stackrel{\circ}{O}$  $H$  +  $H^+$  — $\stackrel{\circ}{M}$  $R$ — $\stackrel{\circ}{O}$  $H_2$   
Alcohol Oxonium salt (Less stable)

c. Since N being less electronegative can accommodate the positive charge better than the more electronegative O-atom, therefore, ammonium salts are more stable than oxonium salts. As a result, amines are more basic than alcohols.

