Padasalai’s Telegram Groups!

(தலைப்புத் தீர்த்த மலர் விளக்கம் கிளிக்கும் முடியும் தமிழ் படைப்புடன்!)

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1. What is inert pair effect?
In heavier post-transition metals, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect. This effect is also observed in groups 14, 15 and 16.

2. Chalcogens belongs to p-block. Give reason.
   i) The chalcogens are the first group in the p block to have no stable metallic elements.
   ii) All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal.
   iii) As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

3. Explain why fluorine always exhibit an oxidation state of -1?
   1. fluorine the most electronegative element, also behaves quiet differently compared to the rest of the members of group
   2. Absence of d orbitals in their valance shell
   3. The fluorine is the strongest oxidising agent and the most reactive element among the halogens.

4. Give the oxidation state of halogen in the following.
   a) $\text{OF}_2$
   b) $\text{O}_2\text{F}_2$
   c) $\text{Cl}_2\text{O}_3$
   d) $\text{I}_2\text{O}_4$

   Fluorine shows only -1 oxidation state

   a) $\text{OF}_2$
   
   \[ 2 + 2x = 0 \]
   \[ 2x = -2 \]
   \[ x = -1 \]

   b) $\text{O}_2\text{F}_2$
   
   \[ 2(1) + 2x = 0 \]
   \[ 2 - 2x = 0 \]
   \[ 2x = -2 \]
   \[ x = -1 \]

   c) $\text{Cl}_2\text{O}_3$
   
   \[ 2x + 3(-2) = 0 \]
   \[ 2x - 6 = 0 \]
   \[ 2x = 6 \]
   \[ X = 3 \]

   d) $\text{I}_2\text{O}_4$
   
   \[ 2x + 4(-2) = 0 \]
   \[ 2x - 8 = 0 \]
   \[ 2x = 8 \]
   \[ X = 4 \]

   **Oxidation state of Cl is +3**
   **Oxidation state of I is +4**

5. What are interhalogen compounds? Give examples.
Each halogen combines with other halogens to form a series of compounds called inter halogen compounds.

   A is less electronegative than B.
   
   AB type - ClF, BrF
   AB₃ type - BrF₃
   AB₅ type - IF₅
   AB₇ type - IF₇
6. Why fluorine is more reactive than other halogens?
   Fluorine is more reactive.

   Due to very small size of F there is inter electronic repulsion in \( F_2 \).

   This is due to the low value of F-F bond dissociation energy.

   Fluorine wants to get to a stable 10 electrons to be like Neon.

   This is because the valence/bonding electrons are closer to the nucleus in Fluorine than they are
   Chlorine and others and thus more strongly attracted

   Fluorine is most electronegative, thus it is most reactive.

7. Give the uses of helium.
   i). Helium is used to provide inert atmosphere in electric arc welding of metals
   ii). Helium has lowest boiling point hence used in cryogenics (low temperature science).
   iii) It is much less denser than air and hence used for filling air balloons

8. What is the hybridisation of iodine in \( IF_7 \)? Give its structure.
   Iodine atom undergoes sp\(^3\)d\(^3\) hybridization to give 7 half filled sp\(^3\)d\(^3\) hybrid orbitals in
   pentagonal bipyramidal symmetry. shape of \( IF_7 \) is pentagonal bipyramidal.

   F-I-F bond angles in the pentagonal plane are equal to 72°

   ![Iodine diagram]

   Geomentry of \( IF_7 \) is pentagonal bipyramidal.
9. Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH.
   i) Cold dilute alkali to give chloride and hypochlorite
      
      \[2\text{NaOH}_{(aq)} + \text{Cl}_2 \rightarrow \text{NaCl}_{(aq)} + \text{NaOCl} + \text{H}_2\text{O}\]
   
   ii) Hot concentrated alkali to give chlorides and chlorates are formed.
      
      \[6\text{NaOH}_{(aq)} + 3\text{Cl}_2 \rightarrow 5\text{NaCl}_{(aq)} + \text{NaClO}_3 \text{ (aq)} + 3\text{H}_2\text{O} \text{ (l)}\]

10. How will you prepare chlorine in the laboratory?
    Chlorine can also be prepared by dripping concentrated hydrochloric acid on KMnO₄ crystals:
    
    \[2\text{KMnO}_4 + 16\text{HCl} \rightarrow 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 5\text{Cl}_2\]

11. Give the uses of sulphuric acid.
    1. Sulphuric acid is used in the manufacture of fertilisers, ammonium sulphate and super phosphates and other chemicals such as hydrochloric acid, nitric acid etc...
    2. It is used as a drying agent and also used in the preparation of pigments, explosives etc..

12. Give a reason to support that sulphuric acid is a dehydrating agent.
    i) It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent.
    ii) When dissolved in water, it forms mono (H₂SO₄·H₂O) and dihydrates (H₂SO₄·2H₂O) and the reaction is exothermic

    Example: \[\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{SO}_4 \rightarrow 12\text{C} + \text{H}_2\text{SO}_4·11\text{H}_2\text{O}\]

13. Write the reason for the anomalous behaviour of Nitrogen.
    i) Small size of N atom.
    ii) High value of electronegativity of N atom and high ionization energy.
    iii) Absence of d-orbitals in the valency shell.
    iv) Tendency of form multipole bonds.
    v) As a result the catenation tendency is weaker in nitrogen

14. Write the molecular formula and structural formula for the following molecules.
    a) Nitric acid  b) dinitrogen pentoxide  c) phosphoric acid  d) phosphine

    | Name           | Molecular Formula | Structure                        |
    |----------------|-------------------|----------------------------------|
    | a) Nitric acid | HNO₃              | ![Nitric acid structure]         |
    | b) dinitrogen pentoxide | N₂O₅        | ![Dinitrogen pentoxide structure] |
    | c) phosphoric acid | H₃PO₄      | ![Phosphoric acid structure]     |
    | d) phosphine   | PH₃             | ![Phosphine structure]           |

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15. Give the uses of argon.
   Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs

16. Write the valence shell electronic configuration of group-15 elements.
   The general valence shell electronic set up of group fifteen elements is ns², np¹⁻⁶

17. Give two equations to illustrate the chemical behaviour of phosphine.
   Basic nature: Phosphine is weakly basic and forms phosphonium salts with halogen acids.
   \[ \text{PH}_3 + \text{HI} \rightarrow \text{PH}_4\text{I} \]
   Reducing property: Phosphine precipitates some metal from their salt solutions.
   \[ 3\text{AgNO}_3 + \text{PH}_3 \rightarrow \text{Ag}_3\text{P} + 3\text{HNO}_3 \]

18. Give a reaction between nitric acid and a basic oxide.
   Nitric acid react with zinc oxide to produce zinc nitrate and water.
   \[ 2\text{HNO}_3 + \text{ZnO} \rightarrow \text{Zn(NO}_3)_2 + \text{H}_2\text{O} \]
   Magnesium react with nitric acid to produce nitrate magnesium and water.
   \[ \text{MgO} + 2\text{HNO}_3 \rightarrow \text{Mg(NO}_3)_2 + \text{H}_2\text{O} \]

19. What happens when PCl₅ is heated?
   \[ \text{PCl}_5(\text{g}) \xrightarrow{\Delta} \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \]

20. Suggest a reason why HF is a weak acid, whereas binary acids of the all other halogens are strong acids.
   HF is the weakest acid because of its strong H-F bond.
   Fluorine being small in size overlaps better with 1s orbital of hydrogen leading to a strong bond.
   Hence can not give proton easily. Here bond strength overweighs the electronegativity of F

21. Deduce the oxidation number of oxygen in hypofluorous acid – HOF.
   \[ \text{H} - \text{O} - \text{F} +1 + x - 1= 0 , x =0 \]
   The oxidation state of the oxygen in hypofluorites is 0.
   It is also the only hypohalous acid that can be isolated as a solid.

22. What type of hybridisation occur in a) BrF₅ b) BrF₃

   b) BrF₅
   Valence electron 7+ bonding electron 5 = 12
   \[ X = \frac{12}{2} = 6 \]
   Hybridization: sp³d²
   Geometry: Square Pyramidal

   b) BrF₃
   Valence electron 7+ bonding electron 3 = 10
   \[ X = \frac{10}{2} = 5 \]
   Hybridization: sp³d
   Geometry: Trigonal Bipyramidal
   Shape - T-shaped
   Lone pair - 2  bond pair - 3

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23. Complete the following reactions.

1. $4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{Cl}_2 + \text{MnCl}_2 + 4\text{NaHSO}_4 + 2\text{H}_2\text{O}$

2. $\text{NaNO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HNO}_2$

3. $\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ \rightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O}$

4. $\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$

5. $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$

6. $3\text{AgNO}_3 + \text{PH}_3 \rightarrow \text{Ag}_3\text{P} + 3\text{HNO}_3$

7. $4\text{Mg} + 10 \text{HNO}_3 \rightarrow 4\text{Mg(NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$

If the acid is diluted we get $\text{N}_2\text{O}_5$

$4\text{Mg} + 10 \text{HNO}_3 \rightarrow 4\text{Mg(NO}_3)_2 + \text{N}_2\text{O}_5 + 5\text{H}_2\text{O}$

8. $2\text{KClO}_3 \xrightarrow{\text{MnO}_2} 2\text{KCl} + 3\text{O}_2$

9. $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$

(Hot Conc.)

10. $2\text{Sb} + 3\text{Cl}_2 \rightarrow 2\text{SbCl}_3$

11. $2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{Br}_2 + \text{SO}_2$

12. $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$

13. $5\text{XeO}_6^{4+} + 2 \text{Mn}^{2+} + 14\text{H}^+ \rightarrow 2\text{MnO}_4^- + 5\text{XeO}_3 + 7\text{H}_2\text{O}$

14. $2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$

15. $\text{Xe} + \text{F}_2 \xrightarrow{\text{Ni} / 200 \text{ atm} \ 400°\text{C}} \text{XeF}_2$

Ans:

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1. **What are transition metals? Give four examples.**

Transition elements that have incompletely filled d sub shell in the neutral or cationic state are called transition metals.

**Four examples.**

- **First (3d):** Ti, V, Cr, Fe
- **Second (4d):** Mo, Ru, Rh, Pd
- **Third (5d):** W, Os, Ir, Pt
- **Fourth (6d):** Db, Sg, Bh, Ds

2. **Explain the oxidation states of 4d series elements.**

   - **a)** At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.
   - **b)** The oxidation states of 4d series elements vary from +3 for Y and +2 to +8 for Ru, Cd for +2.
   - **c)** The highest oxidation state of 4d elements are found in their compounds with the higher electronegative elements like O, F and Cl. For example: RuO$_4$.
   - **d)** Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.

3. **What are inner transition elements?**

The last electron enters into (n - 2) f - orbital which is inner to the penultimate shell, they are also called inner transition elements.

In the inner transition elements there are two series of elements:

1. Lanthanoids (previously called lanthanides (57-71))
2. Actinoids (previously called actinides (89-103))

4. **Justify the position of lanthanides and actinides in the periodic table.**

The actual position of Lanthanoids in the periodic table is at group number 3 and period number 6. However, in the sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties.

Therefore these elements are grouped together and placed at the bottom of the periodic table. This position can be justified as follows.

1. Lanthanoids have general electronic configuration [Xe] 4f$^{1-14}$ 5d$^{0-1}$ 6s$^2$
2. The common oxidation state of lanthanoids is +3
3. All these elements have similar physical and chemical properties.

5. **What are actinides? Give three examples.**

The fourteen elements following actinium, i.e., from thorium (Th) to lawrentium (Lr) are called actinoids.

**Actinide** - These are elements with atomic numbers from 90 to 103.

**Examples.**

- **The 15 elements include:** Actinium (Ac), Thorium (Th), Protactinium (Pa), Uranium (U),
6. Why Gd $^{3+}$ is colourless?

The At.No of Gd is 64. EC is (Xe) 4f$^{7}$ 5d$^{1}$ 6s$^{2}$. In Gd $^{3+}$, they have exactly half filled f-orbitals.

Hence (Xe) 4f$^{7}$5d$^{0}$ 6s$^{0}$. Due to this it is colourless.

7. Explain why compounds of Cu$^{2+}$ are coloured but those of Zn$^{2+}$ are colourless.

1) Zn$^{2+}$ ion has all paired electrons (configuration [Ar] 3d$^{10}$)

Cu$^{2+}$ ion has an unpaired electron (its configuration is [Ar] 3d$^{9}$)

2) i) In case of Zn$^{2+}$ ion fully filled d orbital is present therefore no d-d transition can be possible in this case and it is colorless.

ii) In case of Cu$^{2+}$ ion because of d-d transition electrons emits light in the visible range and hence they are colored compounds.

8. Describe the preparation of potassium dichromate.

Potassium dichromate is prepared from chromate ore. The ore is concentrated by gravity separation.

i) Conversion of Chromate ore into Sodium chromate

$$4\text{FeCr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \underset{900-1000^\circ\text{C}}{\rightarrow} 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$

ii) Conversion of Sodium chromate into Sodium dichromate

$$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

iii) Conversion of Sodium dichromate into Potassium dichromate

$$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$$

9. What is lanthanide contraction and what are the effects of lanthanide contraction?

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.

A. Basicity differences

As we move from Ce$^{3+}$ to Lu$^{3+}$, the basic character of Ln$^{3+}$ ions decrease. Due to the decrease in the size of Ln$^{3+}$ ions, the ionic character of Ln - OH bond decreases (covalent character increases) which results in the decrease in the basicity.

B. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. Because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

10. Complete the following

a) $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^{-} + \text{MnO}_2 + 2\text{H}_2\text{O}$

b) $\text{C}_6\text{H}_5\text{CH}_3 + \text{KMnO}_4/\text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{COOH}$

c) $\text{MnO}_4^{-} + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

d) $\text{KMnO}_4 \text{ Red hot } / \Delta \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$

e) $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^{-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$

f) $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$

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11. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen, carbon or nitrogen are trapped in the interstitial holes in a metal lattice.

Example: TiC, ZrH\(_{1.92}\), Mn\(_4\)N etc.

12. Calculate the number of unpaired electrons in Ti\(^{3+}\), Mn\(^{2+}\) and calculate the spin only magnetic moment.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>(n)</th>
<th>(\mu_s = \sqrt{n(n+2)} \mu_B)</th>
<th>(\mu_s) (observed)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{3+})</td>
<td>(d^1)</td>
<td>1</td>
<td>(\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \mu_B)</td>
<td>paramagnetic</td>
<td></td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>(d^5)</td>
<td>5</td>
<td>(\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \mu_B)</td>
<td>paramagnetic</td>
<td></td>
</tr>
</tbody>
</table>

13. Write the electronic configuration of Ce\(^{4+}\) and Co\(^{2+}\).

i) Configuration of Ce\(^{4+}\)  
\[\text{[Xe]} 5d^0 6s^2\]

ii) Configuration of Co\(^{2+}\)  
\[\text{[Ar]} 3d^7 4s^0\]

14. Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

i) All the metals display +2 oxidation states except Sc.

ii) On moving from the Sc to the Mn, the atomic numbers increase from 21 to the 25.

iii) It means the number of electrons in the 3d-orbital also increases from 1 to 5.

\[\begin{align*}
\text{Sc} (+2) &= d^1, \\
\text{Ti} (+2) &= d^2, \\
\text{V} (+2) &= d^3, \\
\text{Cr} (+2) &= d^4, & \text{and} \quad \text{Mn} (+2) &= d^5.
\end{align*}\]

iv) The +2 oxidation state is achieved by loss of the two 4s electrons by the metals. Since the number of d electrons in (+2) state also increases from Ti(+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d\(^5\) electrons.

15. Which is more stable? Fe\(^{3+}\) or Fe\(^{2+}\) - explain.

Fe\(^{3+}\) ion is more stable due to its half-filled 3d\(^5\) electron configuration.

As half filled and completely filled shells are more stable Fe\(^{3+}\) ion is more stable.

While Fe\(^{2+}\) ion is partially filled d sub shell (3d\(^6\)) in not stable. Hence, Fe\(^{3+}\) is more stable than Fe\(^{2+}\).

16. Explain the variation in \(E_{M^{3+}/M^{2+}}^o\) /3d series.

ii) In 3d series as we move from Ti to Zn, the standard reduction potential \((E_{M^{3+}/M^{2+}}^o)\) value is approaching towards less negative value and copper has a positive reduction potential. i.e. elemental copper is more stable than Cu\(^{2+}\).

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ii) In the general trend, \(E^{0}_{M^{3+} / M^{2+}}\)

The value for manganese and zinc are more negative than the regular trend. It is due to extra stability which arises due to the half filled d⁵ configuration in Mn²⁺ and completely filled d¹⁰ configuration in Zn²⁺.

iii) Transition metals in their high oxidation states tend to be oxidizing. For example, Fe³⁺ is moderately a strong oxidant, and it oxidises copper to Cu²⁺ ions.

The feasibility of the reaction is predicted from the following standard electrode potential values.

\[
\begin{align*}
Fe^{3+}(aq) + e^- & \rightleftharpoons Fe^{2+} \quad E^0 = 0.77 \text{ V} \\
Cu^{2+}(aq) + 2e^- & \rightleftharpoons Cu(s) \quad E^0 = +0.34 \text{ V}
\end{align*}
\]

iv) The standard electrode potential for the \(E^{0}_{M^{3+} / M^{2+}}\) half-cell gives the relative stability between M³⁺ and M²⁺.

\[
\begin{align*}
i) \ Ti^{3+} + e^- & \rightarrow Ti^{2+} \quad \text{Standard reduction potential} = -0.37 \text{ V} \\
ii) \ V^{3+} + e^- & \rightarrow V^{2+} \quad \text{Standard reduction potential} = -0.26 \text{ V} \\
iii) \ Cr^{3+} + e^- & \rightarrow Cr^{2+} \quad \text{Standard reduction potential} = -0.41 \text{ V}
\end{align*}
\]

v) The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr³⁺ ion, strong reducing agent which has high negative value for reduction potential like metallic zinc. \((E^0 = -0.76 \text{ V})\) is required.

eg) The high reduction potential of \(M^{3+} / M^{2+}\) indicates Mn²⁺ is more stable than Mn³⁺.

\[
\begin{align*}
Mn^{2+} + 2e^- & \rightarrow Mn \quad E^0_{Mn^{2+} / Mn} = -1.18 \text{ V} \\
Mn^{3+} + e^- & \rightarrow Mn^{2+} \quad E^0_{Mn^{3+} / Mn^{2+}} = +1.51 \text{ V}
\end{align*}
\]

Mn³⁺ has a 3d⁵ configuration while that of Mn²⁺ is 3d⁵. The extra stability associated with a half filled d sub shell makes the reduction of Mn³⁺ very feasible \((E^0 = +1.51 \text{ V})\).

17. Compare lanthanides and actinides.

<table>
<thead>
<tr>
<th>1 Differentiating electron enters in 4f orbital</th>
<th>Differentiating electron enters in 5f orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Binding energy of 4f orbitals are higher</td>
<td>Binding energy of 5f orbitals are lower</td>
</tr>
<tr>
<td>3 They show less tendency to form complexes</td>
<td>They show greater tendency to form complexes</td>
</tr>
<tr>
<td>4 Most of the lanthanoids are colourless</td>
<td>Most of the actinoids are coloured.</td>
</tr>
<tr>
<td></td>
<td>eg) U³⁺(red), U⁴⁺(green), UO₂²⁺(yellow)</td>
</tr>
<tr>
<td>5 They do not form oxo cations</td>
<td>They do form oxo cations such as UO₂²⁺O₂²⁺, etc</td>
</tr>
</tbody>
</table>

18. Explain why Cr²⁺ is strongly reducing while Mn³⁺ is strongly oxidizing.

Cr²⁺ is strongly reducing in nature. It has a d⁴ configuration. While acting as a reducing agent, it gets oxidized to Cr³⁺ (electronic configuration, d³). This d³ configuration can be written as t₂g³ configuration, which is a more stable configuration.

In the case of Mn³⁺ (d⁴), it acts as an oxidizing agent and gets reduced to Mn²⁺ (d⁵). This has an exactly half-filled d-orbital and has an extra-stability.

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19. Compare the ionization enthalpies of first series of the transition elements.

1) As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons.

2) The increase in first ionization enthalpy with increase in atomic number along a particular series is not regular.

3) The added electron enters (n-1)d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values.

4) Chromium has low first ionization enthalpy because lose one electron gives stable configuration (3d⁵⁻) While Zinc has very high ionization enthalpy because electron has to be removed from 4s orbitals.

20. Actinoid contraction is greater from element to element than the lanthanoid contraction, why?

i) In actinoids, 5f orbitals are filled. These 5f orbitals have a poorer shielding effect than 4f orbitals (in lanthanoids).

ii) Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more that than experienced by lanthanoids.

iii) Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

21. Out of Lu(OH)₃ and La(OH)₃ which is more basic and why?

La(OH)₃ is most basic and Lu(OH)₃ is least basic. Due to lanthanide contraction. As the size of lanthanide ions decreases from La³⁺ to Lu³⁺, the covalent character of the hydroxides increases and hence the basic strength decreases.

22. Why europium (II) is more stable than Cerium (II)?

i) Europium (II) is more stable than Cerium (II) As we from left to right, effective nuclear charge increases due to which lanthanide contraction takes place. The inert pair effect becomes more dominative.

ii) In Eu²⁺, 4f sub shell is half filled and Ce²⁺, 4f and 5d sub shells are partially filled so, Eu(II) more stable than Ce(II)
23. Why do zirconium and Hafnium exhibit similar properties?
Zr and Hf exhibit similar properties due to lanthanoid contraction.
Electrons present in f subshell didn't do good shielding due to which with the increasing atomic number or increasing effective nuclear charge size gets constricted.
The size of Halfenium and Zirconium becomes almost equal.

4d series Zr 145 pm
5d Series Hf 144 pm

24. Which is stronger reducing agent Cr\(^{2+}\) or Fe\(^{2+}\)?
Cr\(^{2+}\) is a stronger reducing agent than Fe\(^{2+}\).
This can be explained on the basis of the standard electrode potential values
\[ E^\circ (Cr^{3+}/Cr^{2+} = -0.41 \text{ V}) \quad \text{and} \quad E^\circ (Fe^{3+}/Fe^{2+} = +0.77 \text{ V}). \]
Thus Cr\(^{2+}\) is easily oxidised to Cr\(^{3+}\) but Fe\(^{2+}\) cannot be as readily oxidised to Fe\(^{3+}\).

25. The \( E^\circ_{M^{2+}/M} \) value for copper is positive. Suggest a possible reason for this.
1. Sublimation energy:
The energy needed to convert one mole of atoms from a solid state to gaseous state.
2. Ionization energy:
The energy supplied to remove electrons from one mole of atoms, which are in the gaseous state.
3. Hydration energy:
The energy emitted to hydrate one mole of ions.
Now, Copper has a high energy of atomization and low hydration energy. Hence, the \( E^\circ_{M^{2+}/M} \) value for copper is positive.

26. Predict which of the following will be coloured in aqueous solution Ti\(^{2+}\), V\(^{3+}\), Cu\(^{+}\), Sc\(^{3+}\), Fe\(^{3+}\), Ni\(^{2+}\) and Co\(^{3+}\)
A transition metal ion in coloured if it has one or more unpaired electron in (n-1)d orbitals i.e. 3d orbitals in case of first transition series. When such species are exposed to visible radiation, d-d transition can take place.

( It does not contain unpaired electron in 3d orbitals so it is colourless )

<table>
<thead>
<tr>
<th>ion</th>
<th>configuration</th>
<th>colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{2+})</td>
<td>3d(^{1})4s(^{0})</td>
<td>Violet</td>
</tr>
<tr>
<td>V(^{3+})</td>
<td>3d(^{2})4s(^{0})</td>
<td>Green</td>
</tr>
<tr>
<td>Cu(^{+})</td>
<td>3d(^{10}) 4s(^{0})</td>
<td>colourless</td>
</tr>
<tr>
<td>Sc(^{3+})</td>
<td>3d(^{0})4s(^{0})</td>
<td>colourless</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>3d(^{5})4s(^{0})</td>
<td>brown to yellow</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>3d(^{8})4s(^{0})</td>
<td>green</td>
</tr>
<tr>
<td>Co(^{3+})</td>
<td>3d(^{6})4s(^{0})</td>
<td>blue</td>
</tr>
</tbody>
</table>

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27. Describe the variable oxidation state of 3d series elements.

The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small.

At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

For example, the first element Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.

The relative stability of different oxidation states of 3d metals is correlated with the extra stability of half filled and fully filled electronic configurations. Example: Mn$^{2+}$ ($3d^5$) is more stable than Mn$^{4+}$ ($3d^4$).

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

Cu is the only metal in the first transition series (3d series) which shows +1 oxidation state most frequently. This is because the electronic configuration of Cu is 3d$^{10}$ 4s$^1$ and after losing one electron it acquires a stable 3d$^{10}$ configuration.

29. Why first ionization enthalpy of chromium is lower than that of zinc?

The electronic configuration of Zn and Cr is given below:

Cr = [Ar] 3d$^5$4s$^1$  Zn = [Ar] 3d$^{10}$ 4s$^2$.

First ionisation enthalpy of Cr is lower than that of Zinc because in case of zinc first electron has to be remove from fulfilled orbital and full filled electronic configuration is most stable so it require high energy to remove electron from it. While in case of Chromium electron is easily removed from half filled orbital with less amount of energy.

30. Transition metals show high melting points why?

a) The melting-points of the transition metals are high due to the 3d electrons being available for metallic bonding.

b) This strength of the bond is due to the presence of unpaired or delocalized electrons in the outermost shell of the atom.

c) The enthalpies of atomization and the densities of transition elements are also high that leads to high boiling and melting points.
1. Write the IUPAC names for the following complexes.

   i) Na₂[Ni(EDTA)]
   ii) [Ag(CN)₂]⁻
   iii) [Co(en)₃]₂(SO₄)₃
   iv) [Co(ONO)(NH₃)₅]²⁺
   v) [Pt(NH₃)₂Cl(NO₂)]

   Ans:
   i) Na₂[Ni(EDTA)] - Sodium 2,2’,2”2”’-ethane-1,2-diaminodisartarate nickelate(II)
   ii) [Ag(CN)₂]⁻ - Dicyanidoargentate(I) ion
   iii) [Co(en)₃]₂(SO₄)₃ - tris(ethylenediamine)cobalt(III)sulphate.
   iv) [Co(ONO)(NH₃)₅]²⁺ - pentaamine(nitritoκ-O)cobalt(III)sulphate
   v) [Pt(NH₃)₂Cl(NO₂)] - diamminechloridonitritoκ-N-platinum(II)

2. Write the formula for the following coordination compounds.

   a) potassiumhexacyanidoferrate(II) - K₄[Fe(CN)₆]
   b) pentacarbonyliron(0) - [Fe(CO)₅]
   c) pentaamminenitritocobalt(III) ion - [Co(NH₃)₅NO₂]²⁺
   d) hexaamminecobalt(III) sulphate - [Co(NH₃)₆]₂(SO₄)₃
   e) sodiumtetrafluoridodihydroxidochromate(III) - Na₃[CrF₄(OH)₂]

3. Arrange the following in order of increasing molar conductivity

   i) Mg [Cr(NH₃)₂(Cl)₅]
   ii) [Cr(NH₃)₃]₂[CoF₆]₂
   iii) [Cr(NH₃)₅]Cl₂

   i) Mg [Cr(NH₃)₂(Cl)₅] → Mg²⁺ + [Cr(NH₃)₅]Cl²⁻
   Total no of ions = 2
   ii) [Cr(NH₃)₃]₂[CoF₆]₂ → 3[Cr(NH₃)₂]Cl²⁺ + 2[CoF₆]³⁻
   Total no of ions = 5
   iii) [Cr(NH₃)₅]Cl₂ → no dissociation occurs
   Total no of ions = 0

   More the number of ions given out by the complex on dissociation and their molar conductivity also increases.

   increasing order of molar conductivity

   [Cr(NH₃)₅]Cl₂ < Mg [Cr(NH₃)₂(Cl)₅] < [Cr(NH₃)₅]Cl₂[CoF₆]₂

4. Ni²⁺ is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction

   Addition of an alcoholic solution of dimethylglyoxime to an ammoniacal solution of Ni(II) gives a rose-red precipitate, abbreviated Ni(dmgl)₂:

   \[ \text{[Ni(NH₃)₆]Cl²⁺ (aq) + 2(CH₃CNOH)₂(aq)} \rightleftharpoons \text{Ni[ONC(CH₃)C(CH₃)NOH]}₂(s) + 2\text{NH}_4^+(aq) + 4\text{NH}_3(aq) \]

5. [CuCl₄]²⁻ exists while [CuI₄]²⁻ does not exist why?

   Both the species contains Cu²⁺ ions but only iodide ion (not chloride ion) reduces Cu²⁺ to cuprous iodide and I₂. Hence, [CuI₄]²⁻ does not exist.

   In [CuI₄]²⁻ complex iodide ion reduces Cu²⁺ to Cu⁺ therefore the complex is unstable.

   so, 2CuI₂ → Cu₂I₂ + I₂
Calculate the ratio of \( \frac{[\text{Ag}^+] }{[\text{Ag(NH}_3\text{)}_2]^+} \) in 0.2 M solution of NH\(_3\). If the stability constant for the complex \([\text{Ag(NH}_3\text{)}_2]^+\) is \(1.7 \times 10^7\)

\[
\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3\text{)}_2]^+ \quad (\beta) = 1.7 \times 10^7, \quad [\text{NH}_3] = 0.2M
\]

i) \( (\beta) = \frac{[\text{Ag(NH}_3\text{)}_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} \), \( \frac{[\text{Ag(NH}_3\text{)}_2]^+}{[\text{Ag}^+] \cdot [\text{NH}_3]^2} = \beta \cdot [\text{NH}_3]^2 = 1.7 \times 10^7 \cdot (0.2)^2 = 6.8 \times 10^5 \)

ii) \[ \frac{[\text{Ag}^+]}{[\text{Ag(NH}_3\text{)}_2]^+} = \frac{1}{\beta \cdot [\text{NH}_3]^2} = \frac{1}{6.8 \times 10^5} = 1.47 \times 10^{-5} \]
\[ \text{ratio} = 1.47 \times 10^{-5} \]

7. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

**Used in medicine**

(1) Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning
(2) Cis-platin is used as an antitumor drug in cancer treatment.

**Biologically important coordination compounds.**

i) (RBC) is composed of heme group, which is Fe\(^{2+}\)- Porphyrin complex. It plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.

ii) Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

8. **Based on VB theory explain why \([\text{Cr(NH}_3\text{)}_3]^{3+}\) is paramagnetic, while \([\text{Ni(CN)}_4]^{2-}\) diamagnetic.**

i) Cr is in the +3 oxidation state i.e., d\(^3\) configuration. Also,

\[
\begin{array}{cccc}
3d & 4s & 4p \\
\uparrow \uparrow \uparrow & & \\
\end{array}
\]

Therefore, it undergoes d\(^2\)sp\(^3\) hybridization and the electrons in the 3d orbitals remain unpaired. Hence, **it is paramagnetic in nature.**

ii) In [Ni(CN)]\(^{4-}\), Ni exists in the +2 oxidation state i.e., d\(^8\) configuration.

\[
\text{Ni}^{2+} \text{ ion} \quad \begin{array}{c}
\begin{array}{c}
3d \\
\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\
\end{array} \\
4s \\
\begin{array}{c}
\end{array} \\
4p \\
\begin{array}{c}
\end{array}
\end{array}
\]

CN\(^-\) is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni\(^{2+}\) under goes dsp\(^2\) hybridization.

\[
\begin{array}{c}
\begin{array}{c}
3d \\
\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\
\end{array} \\
4s \\
\begin{array}{c}
\end{array} \\
4p \\
\begin{array}{c}
\end{array}
\end{array}
\]

As there are **no unpaired electrons, it is diamagnetic.**

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9. Draw all possible geometrical isomers of the complex \([\text{Co}(en)_2\text{Cl}_2]^+\) and identify the optically active isomer.

Cis - \([\text{Co}(en)_2\text{Cl}_2]^+\) shows both geometrical as well as optical isomerism.

Its cis form is unsymmetrical,

\[
\text{cis-} \quad \text{[CoCl}_2\text{(en)_2]}^+ \\
\text{Mirror}
\]

Cis-\([\text{Co}(en)_2\text{Cl}_2]^+\) - optically active [Non - superimposable mirror image]

\[
\text{trans-} \quad \text{[CoCl}_2\text{(en)_2]}^+ \\
\text{Mirror}
\]

trans-[Co(en)_2Cl_2]^+ is symmetrical because it contains a plane of symmetry

Hence, optically in active

In total, Three isomers are possible

10. \([\text{Ti(H}_2\text{O)_6}]^{3+}\) is coloured, while \([\text{Sc(H}_2\text{O)_6}]^{3+}\) is colourless - explain.

i) \([\text{Ti(H}_2\text{O)_6}]^{3+}\) is coloured because of configuration is \(\text{Ti}^{3+} - 3d^1\)

\[
\begin{array}{c}
\text{energy} \\
\uparrow \quad \text{eg} \quad \uparrow \\
\downarrow \quad \text{t}_2g \\
\end{array}
\]

\(\text{d-d transition}\)

has one unpaired electron for d-d transition, hence it is coloured

i) \([\text{Sc(H}_2\text{O)_6}]^{3+}\) is colourless because of configuration is Configuration \(\text{Sc}^{3+} - 3d^0\)

No unpaired electron, so d-d transition is not possible hence it is not coloured

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11. Give an example for complex of the type \([ \text{Ma}_2\text{b}_2\text{c}_2 ]\) where \(a, b, c\) are monodentate ligands and give the possible isomers.

The combination are as follows for \([ \text{Ma}_2\text{b}_2\text{c}_2 ]\) are \((a,a)(b,b),(c,c)\) - this means in the octahedral structure of the compound \(a\) lies directly opposite of \(a\), and \(b\) lies opposite of \(b\), same followed for \(c\). these are the five possible combination eg) \([\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{Br})_2]^+\)

![Diagram of Geometrical Isomers](image)

1. \((a,a)(b,c)(b,c)\) -trans
2. \((b,b) (a,c) (a,c )\) -trans
3. \((c,c) (a,b) (a,b)- trans\)
4. \((a,a)(b,b),(c,c)\) - all trans
5. \((a,c)(a,b) ( b,c) - all cis\)

(5th, isomer - shows optical isomerism d and l form)

7 - isomers out of which 5 are geometrical and 2 are optical isomers.

12. Give one test to differentiate \([\text{Co(NH}_3)_5\text{Cl}]\text{SO}_4\) and \([\text{Co(NH}_3)_5\text{SO}_4]\)\text{Cl}.

This can be tested by using \(\text{AgNO}_3\) solution and \(\text{BaCl}_2\)

**Barium chloride test**

i) \([\text{Co(NH}_3)_5\text{Cl}]\text{SO}_4\)\text{(aq)} + \(\text{BaCl}_2\)\text{(aq)} \(\rightarrow\) \(\text{BaSO}_4\text{(ppt)}\)

ii) \([\text{Co(NH}_3)_5\text{SO}_4]\)\text{Cl} \text{(aq)} + \(\text{BaCl}_2\)\text{(aq)} \(\rightarrow\) no reaction

**Silver nitrate test**

i) \([\text{Co(NH}_3)_5\text{Cl}]\text{SO}_4\)\text{(aq)} + \(\text{AgNO}_3\)\text{(aq)} \(\rightarrow\) no reaction

ii) \([\text{Co(NH}_3)_5\text{SO}_4]\)\text{Cl} \text{(aq)} + \(\text{AgNO}_3\)\text{(aq)} \(\rightarrow\) \(\text{AgCl}\)\text{(ppt)}

Hence they give different precipitates with different solutions. Thus they are ionisation isomers.

13. In an octahedral crystal field, draw the figure to show splitting of d orbitals.
14. What is linkage isomerism? Explain with an example.

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.

**Example** - \([\text{Co(NH}_3\text{)}_5(\text{NO}_2)]^{2+}\)

15. Write briefly about the applications of coordination compounds in volumetric analysis.

a) **Colour Tests**
Since many complexes are highly coloured they can be used as colourimetric reagents

   e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}

b) **Gravimetric Analysis**
Here chelating ligands are often used to form insoluble complexes

   e.g. Ni(DMG)_2 and Al(oxine)_3.

c) **Complexometric Titrations and Masking Agents**
An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution,

   e.g. Zn^{2+}, Pb^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}.

Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

16. Classify the following ligand based on the number of donor atoms.

a) NH}_3\text{) - Monodentate : The ligands which have only one donor atom.

b) en - Bidentate ligands: H_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \text{ ethane-1,2-diamine}

Bidentate ligands have two lone pairs and both of which can bond to the central metal ion. Bidentate ligands may be neutral molecules or anions

c) ox^{2-} - Bidentate ligands

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d) triaminotriethylamine - T etradentate ligands:
Tetradentate ligands have two lone pairs and the four lone pair can bond to the central metal ion.

17. Give the difference between double salts and coordination compounds.

i) **Double salts** are molecular compounds which are formed by the evaporation of solution containing 2 or more salts in stoichiometric proportions. They dissociate into their constituent ions in solution.

\[
K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O
\]

ii) **A complex compound** is a compound formed from a lewis acid and a lewis base.
They do not dissociate into its constituent ions in solutions.

\[
Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]
\]

\[K_4[Fe(CN)_6]\] on dissociation gives \(4K^+ + [Fe(CN)_6]^{4-}\). In \[K_4[Fe(CN)_6]\] the individual components lose their identity. The metal of the complex ion is not free in solution unlike the metal in double salt solution.

18. Write the postulates of Werner’s theory.

i) Most of the elements exhibit, two types of valence namely primary valence and secondary valence.

ii) Primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

iii) The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.

iv) The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.

v) Two spheres of attraction around a metal atom/ion in a complex.

1) The inner sphere is known as coordination sphere

2) The outer sphere is called ionisation sphere.
vi) i) The primary valences - non-directional
   ii) Secondary valences - directional

vii) The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence.

- octahedral geometry.
- either tetrahedral or square planar geometry.

19. $[\text{Ni(CN)}_4]^2-$ is diamagnetic, while $[\text{Ni(Cl)}_4]^2-$ is paramagnetic using crystal field theory?

The $[\text{Ni(CN)}_4]^2-$ is a low-spin square planar complex, since it contains the strong-field CN− ligand in it. The oxidation state number of Ni in the complex +2 and the electronic configuration of Ni$^{2+}$ is 3d$^8$.

In the splitting pattern for a square-planar complex, the orbital possess the highest energy, followed by the dxy and orbitals. The dxz and dyz are symmetrically equivalent. All the eight electrons will enter these five orbitals, such that no electron remains unpaired.

This makes the complex diamagnetic.
8. Electrons have high spin.

So, the d^2 and dx^2-y^2 fill with one electron each, then the dxy, dxz, and dyz with one electron each, and then pairing occurs only after that, filling the d^2, dx^2-y^2, and dxy completely. This leaves two unpaired electrons in the t2 orbitals, and thus this complex is paramagnetic with two unpaired electrons, as expected.


In tetrahedral complex metal atom or ion is at the Centre of a tetrahedron and four ligands are at four corners of tetrahedron this type of complex does not exhibit geometrical isomerism since all four ligands are at the equidistance having bond angle 109°28'

OR

Tetrahedral complexes do not show geometrical isomerism because the relative positions of unidentate ligands attached to the central atom are same with respect to each other.

21. Explain optical isomerism in coordination compounds with an example.

The pair of two optically active isomers which are mirror images of each other are called enantiomers. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called ‘d’ (dextro rotatory) and ‘l’ (levo rotatory) forms respectively.

Examples:
The optical isomers of [Co(en)_3]^3+


22. What are hydrate isomers? Explain with an example.

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

For example

[Cr(H_2O)_6]^3+Cl_3 - is a violet colour compound and gives 3Cl^- ions in solution

[CrCl(H_2O)_5]Cl_2.H_2O - is a pale green colour compound and gives 2Cl^- ions in solution

[CrCl_2(H_2O)_4]Cl_2.H_2O is a dark green colour compound and gives one Cl^- ion in solution.

23. What is crystal field splitting energy?

The degenerate d-orbitals (in a spherical field environment) split into two levels i.e., e_g and t_{2g} in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δo.

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24. What is crystal field stabilisation energy (CFSE)?

The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand field \(E_{LF}\) and the isotropic field/barycentre \(E_{iso}\).

\[
\text{CFSE (\Delta E_o) = } \{E_{LF}\} - \{E_{iso}\} \nonumber
\]

\[
= \left\{ nt_{2g}(-0.4) + n_{eg}(0.6)\right\} \Delta o + n_{p}P - \{n'_{p} P\} \nonumber
\]

\(nt_{2g}\) - is the number of electrons in \(t_{2g}\) orbitals
\(n_{eg}\) - is number of electrons in \(eg\) orbitals
\(n_{p}\) - is number of electron pairs in the ligand field
\(n'_{p}\) - is the number of electron pairs in the isotropic field (barycentre).

25. A solution of \([\text{Ni(H}_2\text{O)}_6]^{2+}\) is green, whereas a solution of \([\text{Ni(CN)}_4]^{2-}\) is colorless – Explain.

In \([\text{Ni(H}_2\text{O)}_6]^{2+}\), Ni is +2 state with the configuration is \(3d^8\) i.e it has two unpaired electrons which do not pair up in the presence of the week \(H_2O\) ligand. Hence, it is coloured, For d-d transition, red is absorbed and complementary light emitted is green

In case \([\text{Ni(CN)}_4]^{2-}\) Ni is again in + 2 state with with the configuration is \(3d^8\) but in the presence of the strong CN- ligand, the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless (no d-d transition)

26. Discuss briefly the nature of bonding in metal carbynols.

The metal-carbon bonds in metal carbynols have both \(\sigma\) and \(\pi\) characters.

A \(\sigma\) bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal.

A \(\pi\) bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti- bonding \(\pi\) orbital (also known as back bonding of the carbonyl group).

The \(\sigma\) bond strengthens the \(\pi\) bond and vice-versa.

Thus, a synergic effect is created due to this metal-ligand bonding.

This synergic effect strengthens the bond between CO and the metal.

27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate?

When excess of liquid ammonia is added to an aqueous solution of copper sulphate it gives tetraammine copper (II) sulphate.

\[
\text{CuSO}_4 + 4\text{NH}_3 \rightarrow [\text{Cu(NH}_3)_4]\text{SO}_4
\]

Thus, the coordination entity formed in the process is \([\text{Cu(NH}_3)_4]\text{SO}_4\) is a very stable complex, which does not ionize to give \(\text{Cu}^{2+}\) ions when added to water

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28. On the basis of VB theory explain the nature of bonding in \([\text{Co(C}_2\text{O}_4)_3]^{3-}\)

Cobalt exists in the +3 oxidation state in the given complex.

**Orbitals of Co\(^{3+}\) ion**

- 3d
- 4s
- 4p
- 4d

Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp\(^3\)d\(^2\) or d\(^2\)sp\(^3\) hybridization.

**sp\(^3\)d\(^2\) hybridization of Co\(^{3+}\):**

The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp\(^3\)d\(^2\) orbitals.

Hence, the geometry of the complex is found to be octahedral.

29. What are the limitations of VB theory?

1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal.

30. Write the oxidation state, coordination number, nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex \(K_4[\text{Mn(CN)}_6]\)

\(K_4[\text{Mn(CN)}_6]\) - Potassium hexacyanomanganate(II)

**Oxidation state of manganese** = +2 \(\{4(+1) + x + 6(-1) = 0; \ x = +2\}\)

**Coordination number** = 6

**Nature of ligand** - CN\(^-\) Monodentate ligand

**Magnetic property**: Paramagnetic

\[
\mu = \sqrt{n(n+2)}
\]

\[
\mu = \sqrt{1(1+2)}
\]

\[
\mu = \sqrt{3}
\]

\[
\mu = 1.732 \text{ BM}
\]

**Electronic configuration** - d\(^5\): t\(_{2g}\)^5

---

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1. Identify the product(s) formed when 1-methoxy propane is heated with excess HI. Name the mechanism involved in the reaction.

The carbon-oxygen bond in ethers can be cleaved by heating with HI to form an alcohol and an alkyl halide at 373K. In the case of unsymmetrical ethers which contain two different alkyl groups, the site of cleavage is such that the halide is formed from the alkyl group which is smaller in size.

Thus the products formed in this case are iodomethane and propan-2-ol.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{-OCH} + \text{HI (excess)} \rightarrow \text{CH}_3\text{I} + \text{CH}_3\text{-CH}-\text{CH}_3 \text{OH} \]

i) Name the mechanism involved in the reaction - $S_N$-1 reaction.

In the presence of conc. HI I think $(\text{CH}_3)_2\text{CH}$-OH changes to $(\text{CH}_3)_2\text{CH}$-I. Also since a secondary carbon is present $S_N$ mechanism may occur then the products are different $(\text{CH}_3\text{OH}$ and $(\text{CH}_3)_2\text{CH}$-I).

2. Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI.

1-Ethoxyprop-1-ene reacts with HI to form iodoethane and prop-1-en-1-ol.

\[ \text{C}_2\text{H}_5\text{OCH} = \text{CH} - \text{CH}_3 + \text{HI (one equivalent of HI)} \rightarrow \text{C}_2\text{H}_5\text{-I} + \text{HO} - \text{CH} = \text{CH} - \text{CH}_3 \]

Not easy to break this bond as it is engaged in resonance so

\[ \text{HO} - \text{CH} = \text{CH} - \text{CH}_3 \xrightarrow{\text{Tautomerism}} \text{O} = \text{CH} - \text{CH}_2 - \text{CH}_3 \text{(aldehyde)} \]

3. Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.

\[ \text{CH}_3 - \text{C} = \text{O} + \text{CH}_3\text{MgBr} \rightarrow \text{CH}_3\text{H}_2\text{C}-\text{O-MgBr} \rightarrow \text{H}_2\text{O/H}^+ \rightarrow \text{CH}_3 - \text{CH} - \text{OH} \]

4. What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.

\[ \text{O} \rightarrow \text{C}_6\text{H}_5\text{-C-OCH}_3 + \text{C}_2\text{H}_5\text{-MgBr} \rightarrow \text{C}_6\text{H}_5\text{-C-OCH}_3 - \text{MgBr/CH}_3\text{O}^- \rightarrow \text{O} \text{C}_6\text{H}_5\text{-C-C}_2\text{H}_5 \]

\[ \text{O} \rightarrow \text{C}_6\text{H}_5\text{-C-C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{-MgBr} \rightarrow \text{C}_6\text{H}_5\text{-C-C}_2\text{H}_5 + \text{Mg(OH)Br} \]

3-phenyl-pentan-3-ol

5. Predict the major product, when 2-methyl but-2-ene is converted into an alcohol in each of the following methods.

(i.) Acid catalysed hydration  (ii.) Hydroboration  (iii.) Hydroxylation using bayers reagent

i) 2-methyl but-2-ene is converted into an alcohol in Acid catalysed hydration

\[ \text{H}_3\text{C} = \text{C} - \text{CH}_3 \xrightarrow{\text{H}^+/50\%\text{H}_2\text{O}} \text{C} - \text{CH}_2\text{-CH}_3 \]

follows Markovnikov's rule  2-Methyl-butane - 2-ol

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2-methyl but-2-ene is converted into an alcohol in Hydroboration

\[
\text{H}_3\text{C} = \text{C} - \text{H} + \text{B}_2\text{H}_6 \rightarrow 2(\text{CH}_3)_2\text{CH} - \text{CH}_3\text{B} + \text{OH}^- \quad \text{iii) 3 H}_2\text{O}_2
\]

follows anti Markovnikov’s rule

\[
\text{H}_3\text{C} = \text{C} - \text{H} + (\text{O}) \xrightarrow{\text{Alkaline KMnO}_4} \text{OH} - \text{OH} \quad \text{OH} \quad \text{OH}
\]

2-Methyl-butan-2,3-diol

ii) 2-methyl but-2-ene is converted into an alcohol in Hydroxylation using bayers reagent

6. Arrange the following in the increasing order of their boiling point and give a reason for your ordering

(i) Butan – 2-ol, Butan -1-ol, 2 –methylpropan -2-ol

(ii) Propan -1-ol, propan -1,2,3-triol, propan -1,3 – diol, propan -2-ol

a) Among isomeric alcohols primary alcohols have higher boiling point and the tertiary alcohols have lower boiling points

b) The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

i) increasing order of their boiling point

2 –methyl propan -2-ol < Butan – 2- ol < Butan -1-ol

ii) increasing order of their boiling point

propan -2-ol < Propan -1-ol < propan -1,3 – diol < propan -1,2,3-triol

7. Can we use nucelophiles such as \( \text{NH}_3, \text{CH}_3\text{O}^- \) for the Nucleophilic substitution of alcohols

Because the OH group of the alcohol must be protonated before it can be displaced by a nucleo-phile, only weakly basic nucleophiles (I\(^-\), Br\(^-\), Cl\(^-\)) can be used in the substitution reaction. Moderately and strongly basic nucleophiles (\( \text{NH}_3, \text{RNH}_2, \text{and CH}_3\text{O}^- \)) cannot be used because they too would be protonated in the acidic solution and, once protonated, would no longer be nucleo-philes (\(+ \text{NH}_4^+, \text{RNH}_3^+\)) or would be poor nucleophiles (\( \text{CH}_3\text{OH} \)).

Chopsticks

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8. Is it possible to oxidise t-butyl alcohol using acidified dichromate to form a carbonyl compound.
   i) Tertiary alcohol does not allow for their oxidation because of absence α-hydrogen atom.
   ii) This is why tertiary alcohols are said to be resistant to oxidation. But at elevated temperatures it possible to oxidise, under strong oxidising agent like acidified K₂Cr₂O₇ / H⁺ cleavage of C – C bond takes place to give a mixture of carboxylic acid like formic acid and acetic acid.

9. What happens when 1-phenyl ethanol is treated with acidified KMnO₄.
   \[
   \text{CH}_3\text{C}-\text{CH}_2\text{OH} + \text{KMnO}_4 + \text{H}^+ \rightarrow \text{Acetophenone}
   \]

10. Write the mechanism of acid catalysed dehydration of ethanol to give ethene.
    The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

    **Primary alcohols undergo dehydration by E₂ mechanism**

    **Step 1:** Protonation of ethanol to form ethyl oxonium ion:
    \[
    \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{O}^+\text{H}^-
    \]

    **Step 2:** Formation of carbocation (rate determining step):
    \[
    \text{CH}_3\text{CH}_2\text{O}^+\text{H}^- \rightarrow \text{CH}_3\text{CH}_2\text{H}^+ + \text{H}_2\text{O}
    \]

    **Step 3:** Elimination of a proton to form ethene:
    \[
    \text{CH}_3\text{CH}_2\text{H}^+ \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}^+
    \]

11. How is phenol prepared from
   i) chloro benzene ii) isopropyl benzene
   i) chloro benzene to phenol

   i) chloro benzene to phenol

   \[
   \text{Cl} + \text{NaOH} \rightarrow \text{NaCl} \rightarrow \text{Sodium phenoxide} \rightarrow \text{Phenol}
   \]

   ii) isopropyl benzene phenol

   \[
   \text{H}_3\text{C}-\text{C} = \text{H} + \text{O}_2 \rightarrow \text{Cumene} \rightarrow \text{Cumene hydroperoxide} \rightarrow \text{Phenol} \rightarrow \text{acetone}
   \]
12. Explain Kolbe’s reaction

![Kolbe's reaction diagram]

13. Write the chemical equation for Williamson synthesis of 2-ethoxy – 2-methyl pentane starting from ethanol and 2 – methyl pentan -2-ol

**Step 1: alcohol into alkylhalide**

\[
\text{CH}_3\text{-CH}_2\text{-OH} + \text{HBr} \xrightarrow{\Delta} \text{CH}_3\text{-CH}_2\text{-Br} + \text{H}_2\text{O}
\]

**Step 2: 2-methyl pentan -2-ol into sodium alkoxide**

\[
2\text{CH}_3\text{-CH}_2\text{-CH}_2 \text{-C-} \text{OH} + 2\text{Na} \rightarrow 2\text{CH}_3\text{-CH}_2\text{-CH}_2 \text{-C-} \text{O} \text{Na}^+ + \text{H}_2
\]

**Step 3: sodium alkoxide into 2-ethoxy – 2-methyl pentane**

\[
\text{CH}_3\text{-CH}_2\text{-CH}_2 \text{-C-} \text{O} \text{Na}^+ + \text{CH}_3\text{-CH}_2\text{Br} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2 \text{-C-} \text{OCH}_2\text{-CH}_3 + \text{NaBr}
\]

14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent-2-en-1-ol.

i) aldehyde yield 4- methylpent-2-en-1-ol

\[
\text{CH}_3\text{-CH} \text{-CH} = \text{CH} \text{-CHO}
\]

ii) carboxylic acid yield 4- methylpent-2-en-1-ol

\[
\text{CH}_3\text{-CH} \text{-CH} = \text{CH} \text{-COOH}
\]

iii) ester yield 4- methylpent-2-en-1-ol

\[
\text{CH}_3\text{-CH} \text{-CH} = \text{CH} \text{-COOCH}_3
\]

Aldehyde, carboxylic acid and ester undergoes reduction that yield 4- methylpent-2-en-1-ol

\[
\text{CH}_3\text{-CH} \text{-CH} = \text{CH} \text{-CH}_2\text{OH}
\]

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15. What is metamerism? Give the structure and IUPAC name of metamers of 2-methoxy propane

Metamerism:

It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

For example an ether having molecular formula $C_4H_{10}O$ exhibits following metamers:

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl isopropyl ether</td>
<td>2-methoxy propane</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>Ethoxy ethane</td>
</tr>
<tr>
<td>Methyl propyl ether</td>
<td>1-methoxy propane</td>
</tr>
</tbody>
</table>

Ethoxy ethane and 1-methoxy propane are metamers of 2-methoxy propane.

16. How are the following conversions effected

i) benzyl chloride to benzyl alcohol

\[
\text{CH}_2\text{Cl} \xrightarrow{\text{NaOH} \text{(aq)}} \text{CH}_2\text{OH}
\]

ii) benzyl alcohol to benzoic acid

\[
\text{OH} \xrightarrow{\text{KMnO}_4/\text{H}_2\text{SO}_4} \text{COOH}
\]

17. Complete the following reactions

i) $\text{CH}_3\text{-CH}_2\text{-OH} \xrightarrow{\text{PBr}_3} \text{A (aq)NaOH } \xrightarrow{\text{B Na}} \text{C}$

\[
\text{CH}_3\text{-CH}_2\text{-OH} \xrightarrow{\text{PBr}_3} \text{CH}_3\text{-CH}_2\text{Br} \xrightarrow{\text{(aq)NaOH}} \text{CH}_3\text{-CH}_2\text{OH} \xrightarrow{\text{Na}} \text{CH}_3\text{-CH}_2\text{ONa} + \frac{1}{2}\text{H}_2
\]

A - ethyl bromide  B - ethanol  C - Sodium ethoxide

ii) $\text{C}_6\text{H}_5\text{-OH} \xrightarrow{\text{Zn}} \text{A} \xrightarrow{\text{CH}_3\text{Cl/anhydrous AlCl}_3} \text{B} \xrightarrow{\text{KMnO}_4/\text{H}^+} \text{C}$

\[
\text{C}_6\text{H}_5\text{-OH} \xrightarrow{\text{Zn}} \text{C}_6\text{H}_6 \xrightarrow{\text{CH}_3\text{Cl}} \text{C}_6\text{H}_5\text{-CH}_3 \xrightarrow{\text{KMnO}_4/\text{H}^+} \text{C}_6\text{H}_5\text{-COOH}
\]

A - benzene  B - Toluene  C - Benzoic acid

iii) Anisole $\xrightarrow{\text{t-butylchloride/AlCl}_3} \text{A} \xrightarrow{\text{Cl}_2/\text{FeCl}_3} \text{B} \xrightarrow{\text{HBr}} \text{C}$

\[
\text{A} \text{- 4-tert-butyl-1-anisole} \quad \text{B} \text{- 2-chloro-4-tert-butyl-1-anisole} \quad \text{C} \text{- 2-chloro-4-tert-butyl-1-phenol}
\]
1-(1-methyl-cyclohexyl)-ethanol to nonane-2,8-dione

0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm$^3$ of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.

Monohydric alcohol + CH$_3$Mgl $\xrightarrow{\text{Ethers}}$ CH$_4$

Monohydric alcohol $\xrightarrow{\text{PCC}}$ Carbonyl compound $\xrightarrow{+ \text{ ve silver mirror test}}$

Monohydric alcohol means a alcohol which contains one hydroxyl group. PCC is an oxidising agent which convert alcohols to aldehyde or ketones. Aldehydes show silver mirror test not ketones. So, aldehyde is formed and primary alcohols give aldehyde on oxidation. Secondary alcohols give ketones. Consider the formula of monohydric alcohol is C$_n$H$_{2n+1}$OH. Alcohols react with grignard reagent form alkyl magnesium halide with the evolution of alkane.

\[
\text{C}_n\text{H}_{2n+1}\text{OH} + \text{CH}_3\text{Mgl} \xrightarrow{\text{CH}_4} \text{CH}_4 + \text{C}_n\text{H}_{2n+1}\text{OMgl}
\]

112 cm$^3$ of methane is produced from 0.44 g of alcohol

\[
22400 \text{ cm}^3 \text{ of methane is produced from } \frac{22400 \times 0.44}{112} = 88 \text{ g}
\]

This is the molar mass of alcohol as 1 mole of alcohol which is equivalent to molar mass produces 22400 cm$^3$ of gas at STP.

Molar mass of alcohol = 81 g

Subtract the mass of hydroxyl group from it = 88 - (16 + 1) = 71 g

C$_n$H$_{2n+1}$ = 71 g

Number of carbon can be possible with this molar mass is 5 which comprises mass 60 g and the rest mass is the mass of hydrogen.

So, the formula of alcohol is C$_5$H$_{11}$OH.

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19. Complete the following reactions

   i) Phenol on treatment with acid chlorides gives esters. The acetylation and benzoylation of phenol are called \textbf{Schotten-Baumann reaction.}

   
   

   ii) \( \text{C}_6\text{H}_5-\text{CHCH(OH)CH(CH}_3\text{)}_2 \) on treatment with acid chlorides gives esters. The acetylation and benzoylation of phenol are called \textbf{Schotten-Baumann reaction.}

20. Phenol is distilled with Zn dust followed by Friedel–Crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A, B and C.

   i) Phenol to benzene

   \[
   \text{Phenol} \xrightarrow{\Delta, \text{Zn}} \text{Benzene} + \text{ZnO}
   \]

   A- benzene
   B- Cumene
   C- Cumene hydro peroxide

   ii) benzene to phenol

   \[
   \text{Benzene} + \text{AlCl}_3 \xrightarrow{\text{Cl}_2} \text{Cumene} \xrightarrow{\text{Air O}_2, 5\% \text{aq Na}_2\text{CO}_3} \text{Cumene hydroperoxide} \xrightarrow{\text{H}_2\text{SO}_4} \text{Phenol} + \text{CH}_3\text{COCH}_3
   \]
21. Identify A, B, C, D and write the complete equation.

\[
\begin{align*}
CH_3MgBr &+ H_3O^+ \rightarrow A \\
&\text{HBr} \rightarrow B \\
&\text{Mg/ether} \rightarrow C \\
&\text{HCHO/H}_3O^+ \rightarrow D
\end{align*}
\]

A - 1-methyl-cyclohexanol
B - 1-bromo-1-methyl-cyclohexane
C - (1-methyl-cyclohexyl) Magnesium bromide
D - (1-methyl-cyclohexyl) methanol

22. What will be the product (X and A) for the following reaction?

\[
\begin{align*}
\text{acetylchloride} &\xrightarrow{\text{i) CH}_3\text{MgBr}} X \\
&\xrightarrow{\text{ii) H}_2O^+} \text{acid K}_2\text{Cr}_2O_7 \rightarrow A
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{COCl} &\xrightarrow{\text{i) CH}_3\text{MgBr}} \text{CH}_3\text{COCH}_3 \\
&\xrightarrow{\text{ii) H}_2O^+} \text{acid K}_2\text{Cr}_2O_7 \rightarrow \text{CH}_3\text{-COOH} + \text{H-COOH}
\end{align*}
\]

X - Acetone
A - Acetic acid

23. How will you convert acetylene into n-butyl alcohol.

\[
\begin{align*}
\text{H-C} &\equiv \text{C-H} \xrightarrow{42\% \text{H}_2\text{SO}_4 / 1\% \text{Hg}^{2+}} \text{CH}_3\text{-COCH}_3 \\
\text{Aldol condensation} \\
\text{step-2} : \text{CH}_3\text{-C} &\equiv \text{CH}_3 + \text{H-CH}_2\text{-CO-CH}_3 \xrightarrow{\text{NaOH}} \text{CH}_3\text{-CH} - \text{CH}_2\text{-CHO} \text{aldol} \\
\text{step-3} : \text{CH}_3\text{-CH} &\equiv \text{CH} - \text{CHO} \xrightarrow{\Delta} \text{CH}_3\text{-CH} = \text{CH} - \text{CHO} + \text{H}_2\text{O} \\
\text{step-4 Reduction of crotonaldehyde to n-butyl alcohol.} \\
\text{CH}_3\text{-CH} = \text{CH} - \text{CHO} \xrightarrow{\text{H}_2/\text{Ni}} \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}
\end{align*}
\]

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24. Predict the product A, B, X and Y in the following sequence of reaction

\[
\text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_3 \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_2\text{Cl} \xrightarrow{\text{Mg/Ether}} \text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_3\text{MgCl} \\
\text{Cu} / 573K \xrightarrow{} \text{CH}_3\text{-CH}_2\text{-CH}\text{-CH}_3
\]

**Compound- A :** 2- chloro - butane  
**Compound- B :** 2- butanone  
**Compound- X :** 2- butanone  
**Compound- Y :** 3, 4-dimethyl-hexan-3-ol

25. 3,3 – dimethylbutan-2-ol on treatment with conc. \( \text{H}_2\text{SO}_4 \) to give tetramethyl ethylene as a major product. Suggest a suitable mechanism

The mechanism is as follows:

**Step-1: protonation of 3,3-dimethylbutan-2-ol**

\[
\text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_3 \xrightarrow{H^+} \text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_3 \text{H}^+ \quad \text{OH}_2
\]

**2) Removal of a water molecule from the carbonium ion formed above**

\[
\text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_3 \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{-CH}_2\text{-CH}-\text{CH}_3^+ \text{H}_3\text{C}
\]

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3) Conversion of 2 degree carbonium to 3 degree carbonium by methyl shift:

\[
\begin{align*}
\text{CH}_3 & \quad \text{+} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{CH} \quad \text{CH}_3 \\
2^\circ \text{-Carbocation} & \quad \text{Methyl shift} \quad \rightarrow \\
\text{CH}_3 & \quad \text{C} \quad \text{CH} \quad \text{CH}_3 \\
3^\circ \text{-Carbocation} &
\end{align*}
\]

4) Removal of H\(^+\) ion to form a double bond:

\[
\begin{align*}
\text{a) CH}_3 & \quad \text{C} \quad \text{CH} \quad \text{CH}_3 \\
\text{b) CH}_3 & \quad \text{C} \quad \text{CH} \quad \text{CH}_3
\end{align*}
\]

\[\beta\text{-Elimination}\]

- H\(^+\)

2,3-dimethyl but-1-ene
( two alkyl substitution )
33 %

Tetra methyl ethylene

2,3-dimethyl but-2-ene
( four alkyl substitution )
64%
major product

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1. Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC names

i) $CH_3-CH_2-CH_2-CH_2-NO_2$  
ii) $CH_3-CH_2-CH_2-CH_2-O - N = O$

iii) $CH_3 - CH - CH_2 - CH_3$  
iv) $CH_3 - CH - CH_2 - CH_3$

v) $CH_3 - CH - CH_2 - NO_2$  
v) $CH_3 - CH - CH_2 - O-N=O$

vi) $CH_3 - CH - CH_2 - CH_3$  
vii) $CH_3 - C - NO_2$

viii) $CH_3 - C - O-N=O$

i) 1-nitro butane  
ii) 1-nitrosooxybutane

iii) 2- nitro butane  
iv) 2-nitro oxy butane

vi) 2- methyl - 1- nitro propane  
vii) 2- methyl -1-nitroso oxy propane

vii) 2- methy-2-nitro propane  
viii ) 2-methyl-2-nitroso oxy propane

2. There are two isomers with the formula $CH_3NO_2$ How will you distinguish between them?

Tautomerism:
Primary and secondary nitroalkanes, having $\alpha$-H, also show an equilibrium mixture of two tautomers namely nitro and aci-form

Distinguish between two form

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Nitro form</th>
<th>Aci – form</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Less acidic</td>
<td>More acidic and also called pseudoacids (or) nitronic acids</td>
</tr>
<tr>
<td>2.</td>
<td>Dissolves in NaOH slowly</td>
<td>Dissolves in NaOH instantly</td>
</tr>
<tr>
<td>3.</td>
<td>Decolourises FeCl$_3$ solution</td>
<td>With FeCl$_3$ gives reddish brown colour</td>
</tr>
<tr>
<td>4.</td>
<td>Electrical conductivity is low</td>
<td>Electrical conductivity is high</td>
</tr>
</tbody>
</table>
3. What happens when
   i. 2 - Nitropropane boiled with HCl
   ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.
   iii. Oxidation of tert - butylamine with KMnO₄
   iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.

   i. 2 - Nitropropane boiled with HCl
   \[ \text{CH}_3\text{-CH-NO}_2 \xrightarrow{\text{boiling HCl}} \text{CH}_3\text{-C}=\text{O} + \text{N}_2\text{O} + \text{H}_2\text{O} \]
   Acetone

   ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.

   iii) Oxidation of tert - butylamine with KMnO₄
   \[ \text{CH}_3\text{-C-CH}_3\text{-NH}_2 + (O) \xrightarrow{\text{KMnO}_4(aq)} \text{CH}_3\text{-C-N}_2\text{O} + \text{H}_2\text{O} \]

   iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.
   Oxidation of acetoneoxime with trifluoroperoxy acetic acid gives 2 - nitropropane \((2^0)\) respectively.

   \[ \text{CH}_3\text{-C} = \text{N-CH}_3\text{-OH} + (O) \xrightarrow{\text{CF}_3\text{-COOH}} \text{CH}_3\text{-C} = \text{NO}_2 + \text{H}_2\text{O} \]
   2 - nitropropane \((2^0)\)

4. How will you convert nitrobenzene into
   i. 1,3,5 - trinitrobenzene
   ii. o and p- nitrophenol
   iii. m - nitro aniline
   iv. azoxybenzene
   v. hydrozobenzene
   vi. N - phenylhydroxylamine
   vii. aniline

   i) Conversion of nitrobenzene into 1,3,5 - trinitrobenzene

   \[ \text{NO}_2 \xrightarrow{\text{Nitrification} 473K} \text{1,3,5 - trinitrobenzene (TNB)} \]

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iii) Conversion of nitrobenzene into m-nitro aniline

\[
\text{C}_6\text{H}_5-\text{NO}_2 + 6\text{[H]} \xrightarrow{\text{Zn} / \text{NaOH} \text{ basic medium}} \text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5 \xrightarrow{2\text{[H]}} \text{C}_6\text{H}_5-\text{NH}=\text{NH}-\text{C}_6\text{H}_5
\]

iv) Conversion of nitrobenzene into N-phenylhydroxylamine aniline

\[
\text{C}_6\text{H}_5-\text{NO}_2 + 2\text{[H]} \xrightarrow{\text{Zn} / \text{NH}_4\text{Cl} \text{ Neutral medium}} \text{C}_6\text{H}_5-\text{NH}-\text{OH} + \text{ZnO}
\]

iv) Conversion of nitrobenzene into aniline

\[
\text{C}_6\text{H}_5-\text{NO}_2 + 6\text{[H]} \xrightarrow{\text{Sn} / \text{HCl} \text{ Acid medium}} \text{C}_6\text{H}_5-\text{NH}_2
\]
5. Identify compounds A, B, and C in the following sequence of reactions.

i) \( \text{C}_6\text{H}_5-\text{NO}_2 + \text{Fe} + \text{HCl} \rightarrow \text{A} \rightarrow \text{HNO}_2/273\text{K} \rightarrow \text{B} \rightarrow \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C} \)

\( \text{Ans:} \quad \text{C}_6\text{H}_5-\text{NO}_2 + \text{Fe} + \text{HCl} \rightarrow \text{C}_6\text{H}_5-\text{NO}_2 \rightarrow \text{HNO}_2/273\text{K} \rightarrow \text{C}_6\text{H}_5-\text{N}_2\text{Cl} \)

Coupling reaction

\( \text{C}_6\text{H}_5\text{OH} \rightarrow \text{p- hydroxy azobenzene} \)

A- Aniline  B- Benzene diazonium chloride  C- p- hydroxy azobenzene

ii) \( \text{C}_6\text{H}_5-\text{N}_2\text{Cl} + \text{CuCN} + \text{H}_2\text{O}/\text{H}^+ \rightarrow \text{A} \rightarrow \text{NH}_3 \rightarrow \text{B} \rightarrow \text{C}_6\text{H}_5-\text{CONH}_2 \)

\( \text{Ans:} \quad \text{C}_6\text{H}_5-\text{N}_2\text{Cl} + \text{CuCN} \rightarrow \text{C}_6\text{H}_5-\text{CN} \rightarrow \text{H}_2\text{O}/\text{H}^+ \rightarrow \text{C}_6\text{H}_5-\text{COOH} \rightarrow \text{NH}_3 \rightarrow \text{C}_6\text{H}_5-\text{CONH}_2 \)

A- Cyanobenzene  B- Benzoic acid  C- Benzamide

---

iii) \( \text{CH}_3-\text{CH}_2-\text{I} + \text{NaCN} + \text{A} + \text{OH}^- \rightarrow \text{B} + \text{NaOH} + \text{Br}_2 \rightarrow \text{C} \)

\( \text{Ans:} \quad \text{CH}_3-\text{CH}_2-\text{I} + \text{NaCN} \rightarrow \text{CH}_3-\text{CH}_2-\text{CN} \rightarrow \text{OH}^- \rightarrow \text{CH}_3-\text{CH}_2-\text{CONH}_2 \rightarrow \text{NaOH} + \text{Br}_2 \rightarrow \text{CH}_3-\text{NH}_2 \)

A- Ethyl cyanide  B- Acetamide  C- Methyl amine

---

iv) \( \text{CH}_3-\text{NH}_2 + \text{CH}_3\text{Br} \rightarrow \text{A} \rightarrow \text{CH}_3\text{COCl} \rightarrow \text{B} \rightarrow \text{C}_2\text{H}_6 \rightarrow \text{C} \)

\( \text{Ans:} \quad \text{CH}_3-\text{NH}_2 + \text{CH}_3\text{Br} \rightarrow (\text{CH}_3)_2\text{NH} + \text{CH}_3\text{COCl} \rightarrow (\text{CH}_3)_2\text{N}-\text{CO}-\text{CH}_3 \rightarrow \text{B}_2\text{H}_6 \rightarrow (\text{CH}_3)_2\text{N}-\text{CH(OH)}-\text{CH}_3 \)

A- N,N dimethyl amine  B- N,N-dimethyl acetamide  C- N,N-dimethyl 2- hydroxy ethan amine

---

v) \( \text{C}_6\text{H}_5-\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} + \text{pyridine} \rightarrow \text{A} \rightarrow \text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow \text{B} \rightarrow \text{H}_2\text{O}/\text{H}^+ \rightarrow \text{C} \)

\( \text{Ans:} \quad \text{C}_6\text{H}_5-\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} + \text{pyridine} \rightarrow \text{C}_6\text{H}_5-\text{NH}_2 \rightarrow \text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5-\text{NH}_2 \rightarrow \text{H}_2\text{O}/\text{H}^+ \rightarrow \text{C}_6\text{H}_5-\text{NH}_2 \)

A- Acetanilide  B- p- nitroacetanilide  C- p- nitro aniline

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i) Hofmann’s bromide reaction
ii. Ammonolysis
iii. Gabriel phthalimide synthesis
iv. Schotten - Baumann reaction
v. Carbylamine reaction
vi. Mustard oil reaction
vii. Coupling reaction
viii. Diazotisation
ix. Gomberg reaction

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i. Hofmann's bromide reaction
When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

\[ \text{CH}_3\text{-CONH}_2 + \text{Br}_2/\text{KOH} \rightarrow \text{CH}_3\text{-NH}_2 + \text{K}_2\text{CO}_3 + \text{KBr} + \text{H}_2\text{O} \]

ii. Ammonolysis
When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1\textsuperscript{st}, 2\textsuperscript{nd} and 3\textsuperscript{rd} amines and quaternary ammonium salts are obtained.

\[ \text{CH}_3\text{-Br} + \text{NH}_3/A \rightarrow \text{CH}_3\text{-NH}_2 \quad \text{1\textsuperscript{st} amine} \]
\[ \text{CH}_3\text{-Br} \rightarrow (\text{CH}_3)_2\text{-NH} \quad \text{2\textsuperscript{nd} amine} \]
\[ \text{CH}_3\text{-Br} \rightarrow (\text{CH}_3)_3\text{-N} \quad \text{3\textsuperscript{rd} amine} \]
\[ \text{CH}_3\text{-Br} \rightarrow (\text{CH}_3)_4\text{N}^+\text{Br}^- \quad \text{Quatertary ammonium bromide} \]

iii. Gabriel phthalimide synthesis
Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide.

![Diagram of Gabriel phthalimide synthesis]

iv. Schotten - Baumann reaction
Aniline reacts with benzoylchloride (C\textsubscript{6}H\textsubscript{5}COCl) in the presence of NaOH to give N-phenyl benzamide. This reaction is known as Schotten - Baumann reaction.

\[ \text{C}_6\text{H}_5\text{-NH}_2 + \text{C}_6\text{H}_5\text{-Cl} \rightarrow \text{C}_6\text{H}_5\text{-NH} - \text{C} - \text{C}_6\text{H}_5 + \text{HCl} \]

v. Carbylamine reaction
Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamines test. This test used to identify the primary amines.

\[ \text{C}_2\text{H}_5\text{-NH}_2 + 3\text{KOH} + \text{CHCl}_3 + \text{Br}_2/\text{KOH} \rightarrow \text{C}_2\text{H}_5\text{-NC} + 3\text{KCl} + 3\text{H}_2\text{O} \]

carbylamines

vi. Mustard oil reaction
i) When primary amines are treated with carbon disulphide (CS\textsubscript{2}), N - alkyl dithiocarbamic acid is formed which on subsequent treatment with HgCl\textsubscript{2} give an alkyl isothiocyanate.

\[ \text{CH}_3 - \text{N} - \text{H} + \text{C} = \text{S} \rightarrow \text{CH}_3 - \text{NH} - \text{C} - \text{SH} \rightarrow \text{CH}_3 - \text{N} = \text{C} = \text{S} + \text{H}_2\text{S} + 2\text{HCl} \]

Methyl isothiocyanate
(Mustard oil smell)

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vii. **Coupling reaction**
Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds.

\[
\text{Phenol} + \text{N}_2\text{Cl}^- + \text{OH}^- \xrightarrow{pH (9-10)} \text{p-hydroxy azo} \text{benzene (orange dye)}
\]

viii. **Diazotisation**
Aniline reacts with nitrous acid at low temperature (273 - 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes seven at low temperatures. This reaction is known as **diazotization**.

\[
\text{Aniline} + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{273 - 278K} \text{Benzenediazonium chloride}
\]

ix. **Gomberg reaction**
Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction is known as the Gomberg reaction.

\[
\text{Benzene diazonium chloride} + \text{NaOH} \xrightarrow{\text{NaOH}} \text{Biphenyl} + \text{N}_2 + \text{HCl}
\]

7. **How will you distinguish between primary secondary and tertiary alphatic amines.**

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Primary amine</th>
<th>Secondary amine</th>
<th>Tertiary amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>With HNO(_2)</td>
<td>forms alcohol</td>
<td>N-nitroso amine</td>
<td>forms salt.</td>
</tr>
<tr>
<td>With CH(_3)Cl/KOH</td>
<td>forms carbylamine</td>
<td>No reaction.</td>
<td>No reaction</td>
</tr>
<tr>
<td>With CS(_2) and HgCl(_2)</td>
<td>alkyl isothiocyanate is formed</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
<tr>
<td>With Diethyl oxalate</td>
<td>dialkyl oxamide, a solid at room temperature is formed.</td>
<td>Forms N,N-dialkyl oxamic ester, a liquid.</td>
<td>No reaction</td>
</tr>
<tr>
<td>With acetyl chloride</td>
<td>forms N-alkyl acetamide.</td>
<td>form N,N-dialkyl acetamide</td>
<td>No reaction</td>
</tr>
</tbody>
</table>

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8. Account for the following

i. Aniline does not undergo Friedel-Crafts reaction

Friedel-Crafts reaction is carried out in the presence of AlCl$_3$, but AlCl$_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl$_3$ to form a salt.

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines

In diazonium salt, the structure goes under resonance due to which the dispersal of positive charge is more and we know that higher is the resonance higher is the stability. Therefore diazonium salt of aromatic amines is more stable than those of aliphatic amines.

iii. $pK_b$ of aniline is more than that of methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate. On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, $pK_b$ of aniline is more than that of methylamine.

iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

v. Ethylamine is soluble in water whereas aniline is not

Ethylamine when added to water forms intermolecular H-bonds with water. And therefore it is soluble in water. But aniline does not form H-bond with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.

vi. Amines are more basic than amides

The lone pair of electrons on the amine are more available to accept a proton and act as a base. This is because in amides, the carbonyl (C=O) group is highly electronegative, so has a greater power to draw electrons towards it, making the lone pair of the amide nitrogen less available to accept a proton.
vii. Although amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

![Aniline, Anilinium, m-Nitroaniline Diagram]

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

9. Arrange the following

i. In increasing order of solubility in water, \( C_6H_5NH_2, (C_2H_5)_2NH, C_2H_5NH_2 \)

The more extensive the H-bonding, the higher is the solubility. Thus, \( C_6H_5NH_2 \) undergoes more extensive H-bonding than \((C_2H_5)_2NH\) \( \). Hence, the solubility in water of \( C_6H_5NH_2 \) is more than that of \((C_2H_5)_2NH\).

\[ C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2 \]

ii. In increasing order of basic strength

a) aniline, p-toluidine and p-nitroaniline

![Basic Strength Diagram]

\( p\)-nitroaniline < aniline < p-toluidine

In p-toluidine, the presence of electron-donating -CH\(_3\) group increases the electron density on the N-atom. Thus, p-toluidine is more basic than aniline. -NO\(_2\) group decreases the electron density over the N-atom in p-nitroaniline. Thus, p-nitroaniline is less basic than aniline.

b) In increasing order of basic strength \( C_6H_5NH_2, C_6H_5NHCH_3, p-Cl-C_6H_4NH_2 \).

i) Chlorine atom has both - I effect and + R effect so para chloro aniline is less basic than aniline

\( CH\(_2\)\) group is electron donating group in so increases electron density in N-atom so, N-Methyl aniline is more basic than aniline

\( p-Cl-C_6H_4NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3 \)

iii. In decreasing order of basic strength in gas phase

\( C_2H_5NH_2, (C_2H_5)_2NH, (C_2H_5)_3N \) and \( NH_3 \)

In gas phase there is no hydrogen bonding, therefore stabilization due to hydrogen bonding is not there. Therefore the only effect to determine the strength is the inductive effect. The +I effect increases with increase in the alkyl group. Therefore the basic strength will be the highest in \((C_2H_5)_3N\) and least in \( NH_3 \). Therefore the decreasing order of basic strength in gas phase will be

\( (C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3 \)

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iv. **In increasing order of boiling point C₆H₅OH, (CH₃)₂NH, C₂H₅NH₂**

The electronegativity of O is more than N. Therefore C₆H₅OH forms hydrogen bonding and because of the hydrogen bonding the alcohols will have higher boiling point than the amines with comparable molecular mass. Now between (CH₃)₂NH and C₂H₅NH₂, C₂H₅NH₂ has more hydrogen atom attached to the Nitrogen. Therefore the extent of hydrogen bonding will be more in primary amines i.e C₂H₅NH₂ as compared to sec or ter amines. Therefore C₂H₅NH₂ will have higher boiling point as compared to (CH₃)₂NH. Therefore the increasing order of boiling point will be as given below.

\[
\text{Ans: } (\text{CH₃})₂\text{NH} < \text{C₂H₅NH₂} < \text{C₆H₅OH}
\]

v. **In decreasing order of the pKₐ values C₂H₅NH₂, C₆H₅NHCH₃, (CH₃)₂NH and CH₃NH₂**

Larger the value of Kb or smaller the value of pKₐ, stronger is the base.

(i) In C₂H₅NH₂, only one -C₂H₅ group is present while in (CH₃)₂NH, two -C₂H₅ groups are present. Thus, the +I effect is more in (C₂H₅)₂NH than in C₂H₅NH₂. Therefore, the electron density over the N-atom is more in C₂H₅NH₂ than in C₂H₅NH₂. Hence, (C₂H₅)₂NH is more basic than C₂H₅NH₂.

(ii) In C₆H₅NHCH₃, less basic than ((CH₃)₂NH and C₂H₅NH₂ due to the delocalization of the lone pair in the former two. Further, among C₆H₅NHCH₃ and (CH₃)₂NH, the former will be more basic due to the +I effect of -CH₃ group. Hence, the order of increasing basicity of the given compounds is as follows:

\[
\text{C₆H₅NHCH₃} < \text{CH₃NH₂} < \text{C₂H₅NH₂} < \text{(C₂H₅)₂NH}
\]

We know that the higher the basic strength, the lower is the pKₐ values.

\[
\text{C₆H₅NHCH₃} > \text{CH₃NH₂} > \text{C₂H₅NH₂} > \text{(C₂H₅)₂NH}
\]

vi. **Increasing order of basic strength C₆H₅NH₂, C₆H₅N(CH₃)₂, (CH₃)₂NH and CH₃NH₂**

C₆H₅N(CH₃)₂ is more basic than C₆H₅NH₂ due to the presence of the + I effect of two -CH₃ group in C₆H₅N(CH₃)₂. Further CH₃NH₂ contains one -CH₃ group while (C₂H₅)₂NH contains two -C₂H₅ group. Thus, (C₂H₅)₂NH is more basic than CH₃NH₂. Now C₆H₅N(CH₃)₂ is less basic than CH₃NH₂ because of the - R effect of -C₆H₅ group. Hence, the increasing order of the basic strength of the given compounds is as follows:

\[
\text{C₆H₅NH₂} < \text{C₆H₅N(CH₃)₂} < \text{CH₃NH₂} < \text{(C₂H₅)₂NH}
\]

vii. **In decreasing order of basic strength**

\[
\text{CH₃CH₂NH₂} > \text{O₂N-} > \text{CH₃ - NH₂} > \text{O₂N-} > \text{CH₃NH₂}
\]

Aliphatic amines are more basic than aromatic amines. So CH₃CH₂NH₂ and CH₃ - NH₂ are more basic. CH₃CH₂NH₂ is more +I effect than CH₃ - NH₂, so CH₃CH₂NH₂ is more basic than CH₃ - NH₂. In case of substituted aniline, electron withdrawing group like -NO₂, they have both -R effect as well as - I effect. As result all nitro amines are weaker bases than aniline.

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10. How will you prepare propan-1-amine from butane nitrile
   i) butane nitrile ii) propanamide ii) 1- nitropropane
   i) Butane nitrile converted into propan-1-amine
      \[
      \text{CH}_3\text{-CH}_2\text{-CH}_2\text{CN} + \text{H}^+ / \text{Hydrolysis} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{CONH}_2
      \]
      \[
      \text{Br}_2 / \text{KOH} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{NH}_2
      \]
   ii) propanamide converted into propan-1-amine
      \[
      \text{CH}_3\text{-CH}_2\text{CONH}_2 \xrightarrow{\text{LiAlH}_4 / \text{H}_2\text{O}} \text{CH}_3\text{-CH}_2\text{-CH}_2\text{NH}_2
      \]
   iii) 1- nitropropane converted into propan-1-amine
      \[
      \text{CH}_3\text{-CH}_2\text{CH}_2\text{NO}_2 \xrightarrow{\text{Sn} / \text{HCl}} \text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{NH}_2 + 2\text{H}_2\text{O}
      \]

11. Identify A,B,C and D

   \[
   \text{CH}_3\text{-NO}_2 \xrightarrow{\text{LiAlH}_4 / 6[\text{H}]} \text{CH}_3\text{NH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{[C}_6\text{H}_5\text{-CH}_2\text{NH}_3^+\text{-C}_6\text{H}_5\text{-CH}_3] \text{HSO}_4^- 
   \]

   A - Methyl amine  
   B - N-Methyl ethan-1-amine
   C - N,N-diethylmethylamine  
   D - Quaternary ammonium hydrogen sulphate

12. How will you convert diethylamine into
   i) N,N-diethylacetamide ii) N- nitrosodiethylamine
   i) Conversion of diethylamine into N,N-diethylacetamide
      \[
      (\text{CH}_3\text{-CH}_2\text{N-H}) \xrightarrow{\text{pyridine}} (\text{CH}_3\text{-CH}_2\text{N-CO}) \text{CH}_3 + \text{HCl}
      \]
   ii) Conversion of diethylamine into N- nitrosodiethylamine
      \[
      (\text{CH}_3\text{-CH}_2\text{N-H}) \xrightarrow{\text{HNO}_2} (\text{CH}_3\text{-CH}_2\text{N=N-O}) \text{C}_6\text{H}_5\text{-CH}_3
      \]

13. Identify A,B and C

   \[
   \text{glutaric acid} \xrightarrow{\text{SOCl}_2} \text{A} \xrightarrow{\text{NH}_3} \text{B} \xrightarrow{\text{LiAlH}_4} \text{(C)} 
   \]

   A - Glutaryl chloride  
   B - Pentanediamide (Glutaramide) 
   C - 1,5 - diaminopentane

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14. Identify A, B, C and D

\[
\text{aniline} + \text{benzaldehyde} \rightarrow A \xrightarrow{\text{Conc HNO}_3} B \quad C \text{ and } D
\]

\[
\begin{align*}
\text{O} & \quad \text{H} & \quad \text{NH}_2 \\
\text{C}_6\text{H}_5 & \quad & \text{C}_6\text{H}_5 \\
\text{N} & \quad \text{O} & \quad \text{H} \\
\text{C}_6\text{H}_5 & \quad & \text{C}_6\text{H}_5 \\
\text{H}_2\text{O} & \quad & \text{H}_2\text{O}
\end{align*}
\]

15. Complete the following reaction

\[
\text{N-benzyl cyclo hexane imine}
\]

16. Predict A, B, C and D for the following reaction

\[
\begin{align*}
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D} \\
\text{NH}_3 & \quad \Delta & \quad \text{i) KOH} & \quad \text{H}_2\text{O} / \text{H}^+ \\
\text{H}_2\text{N} & \quad \text{CH} & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D} \\
\text{NH}_3 & \quad \Delta & \quad \text{KOH} & \quad \text{H}_2\text{O} / \text{H}^+ \\
\text{H}_2\text{N} & \quad \text{CH} & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

Ans:

\[
\begin{align*}
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D} \\
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D}
\end{align*}
\]

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17. A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO₂. (B) on heating with liquid ammonia followed by treating with Br₂/KOH gives (C) which on treating with NaNO₂ and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74. Identify A to D.

\[ \text{i) } \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br} + \text{KCN} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CN} \]

\[ \text{ii) } \text{CH}_3\text{-CH}_2\text{-COOH} + \text{NH}_3 (\text{lig}) \rightarrow \text{CH}_3\text{-CH}_2\text{-CONH}_2 \]

\[ \text{iii) } \text{CH}_3\text{-CH}_2\text{-CONH}_2 + \text{NaNO}_2/\text{HCl} \rightarrow \text{CH}_3\text{-CH}_2\text{-OH} \]

\[ \text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+ \rightarrow \text{CH}_3\text{-CH}_2\text{-COOH} \]

A - 1,2-diamino butane  
B - 1,2-dicyano butane  
C - 1-amino propane  
D - Propanoic acid

Molecular mass of propanoic acid - 74

18. Identify A to E in the following frequency of reactions.

Ans:  
A - Toluene  
B - p-nitro benzene  
C - p-toluidine  
D - p-toluene diazonium salt  
E - p-cyano toluene