

1. Explain:

- (a) (i) The factors responsible for formation of a large number of complexes by transition metals.

- **Reason:**

- **Small Size and High Effective Nuclear Charge:**

Transition metal ions are relatively small in size and possess a high effective nuclear charge. This allows them to attract and hold electron pairs donated by ligands efficiently, leading to strong electrostatic interactions and stable complex formation.

- **Availability of Vacant d-orbitals:** Transition metals have empty or partially filled d-orbitals of appropriate energy. These vacant d-orbitals can accept lone pairs of electrons from ligands to form coordinate bonds. The number of available d-orbitals allows for various coordination numbers and geometries.

- **Variable Oxidation States:** Transition metals exhibit a wide range of oxidation states. This variability allows them to act as Lewis acids (electron acceptors) in different oxidation states, accommodating various ligands and forming diverse complexes.

- **Tendency to Form Covalent Bonds:** In addition to electrostatic interactions, transition metals also show a tendency to form covalent bonds with ligands, especially through π -bonding (e.g., back-bonding in carbonyl complexes), which further stabilizes the complexes.

- (a) (ii) Actinides have a greater tendency to form complexes than lanthanides.

▪ **Reason:**

- **Higher Nuclear Charge and Smaller Ionic Size (for the same oxidation state):** While both series exhibit actinide and lanthanide contraction, actinide ions generally have a higher charge density and slightly smaller ionic radii compared to lanthanide ions of the same oxidation state (especially +3). This leads to stronger electrostatic attraction for ligands.
 - **Lower Shielding of 5f Electrons:** The 5f orbitals in actinides are less effectively shielded from the nuclear charge compared to the 4f orbitals in lanthanides. This means the 5f electrons are more exposed and can participate more readily in bonding with ligands.
 - **Greater Covalent Character:** The more exposed and larger 5f orbitals allow for greater overlap with ligand orbitals, leading to a higher degree of covalent character in the metal-ligand bond in actinide complexes compared to the predominantly ionic bonding in lanthanide complexes. This increased covalent character contributes to greater complex stability.
 - **Availability of Multiple Oxidation States:** Actinides exhibit a wider range of oxidation states (especially higher oxidation states like +4, +5, +6) compared to lanthanides (predominantly +3). Higher oxidation states lead to stronger electrostatic attraction for ligands and thus a greater tendency to form complexes.
- (b) Electronic spectra of Ln^{3+} complexes are similar irrespective of change of ligand.

▪ **Reason:**

- **Deep-seated 4f Orbitals:** In Ln^{3+} ions, the 4f electrons are largely "deep-seated" or inner-core electrons. They are well-shielded from the external environment by the filled 5s and 5p orbitals.
 - **Minimal Ligand Field Effect:** As a result of this effective shielding, the 4f orbitals are not significantly influenced by the electric field generated by the surrounding ligands (the ligand field effect is very weak).
 - **Lack of Ligand-Induced Splitting:** The electronic transitions responsible for the spectra (f-f transitions) occur between different energy levels within the 4f subshell. Since the ligand field has a negligible effect on the splitting of these 4f orbitals, the energy differences between these levels remain largely unchanged regardless of the nature of the ligand.
 - **Sharp, Line-like Spectra:** This weak ligand interaction leads to very sharp, line-like absorption bands in the electronic spectra of Ln^{3+} complexes, which are characteristic of the free ion and are relatively insensitive to the chemical environment.
- (c) The coordination numbers of the elements of second and third transition series tend to be greater than for the first transition series.

▪ **Reason:**

- **Larger Atomic and Ionic Radii:** Elements of the second and third transition series have significantly larger atomic and ionic radii compared to those in the first transition series (due to the presence of an

additional electron shell). This larger size allows them to accommodate a greater number of ligands around the central metal ion without experiencing excessive steric repulsion.

- **Availability of Larger d-orbitals and Lower Energy f-orbitals:** The d-orbitals of the second and third transition series are more diffuse and extended in space, allowing for more effective overlap with ligand orbitals and accommodating more ligands. For third transition series, the involvement of 4f orbitals (due to lanthanide contraction) makes the d-orbitals even more available for bonding compared to 3d orbitals, facilitating higher coordination numbers.
- **Greater Tendency for Covalent Bonding:** The heavier transition metals often exhibit a greater tendency to form covalent bonds, including π -bonding, which can stabilize higher coordination numbers.
- **Relativistic Effects (for 3rd series):** For the third transition series, relativistic effects contribute to the contraction of s-orbitals and expansion of d-orbitals, which can influence bonding characteristics and potentially allow for higher coordination numbers.

2. Explain why:

- (a) (i) Fewer number of oxidation states are available at each end of the first transition series than in the middle?
 - **Reason:**
 - **Early Transition Metals (Sc, Ti):** At the beginning of the first transition series, there are very few d-electrons available. For example, Scandium (Sc)

has a configuration of $3d^1 4s^2$. It can lose all three electrons to achieve a stable +3 oxidation state, but higher oxidation states are not readily available due to the limited number of valence electrons.

- **Middle Transition Metals (Cr, Mn, Fe):** In the middle of the series, both the 3d and 4s orbitals have a sufficient number of electrons that can be involved in bonding. For instance, Manganese (Mn) ($3d^5 4s^2$) can exhibit oxidation states from +2 to +7, utilizing all its valence electrons. This allows for a wider range of possible oxidation states.
 - **Late Transition Metals (Cu, Zn):** Towards the end of the series, the 3d orbitals become increasingly filled. For example, Copper (Cu) is $3d^{10} 4s^1$ and Zinc (Zn) is $3d^{10} 4s^2$. The fully filled d^{10} configuration is very stable. It requires significant energy to remove electrons from these stable, filled d-orbitals. Therefore, the common oxidation states are limited, often to +1 or +2 for copper, and only +2 for zinc, as the inner d-electrons are less available for variable valency.
- (a) (ii) transition metals in high oxidation states are generally available as fluorides or oxides?
- **Reason:**
 - **High Electronegativity of Fluorine and Oxygen:** Both fluorine and oxygen are highly electronegative elements. When transition metals are in high oxidation states, they are highly electron-deficient. To stabilize such a high positive charge, they require ligands that can effectively withdraw electron density and form strong bonds.

- **Small Size of Fluorine and Oxygen:** Fluorine and oxygen atoms are also very small. This small size allows a larger number of them to coordinate around the central metal ion, forming more bonds and thus effectively dispersing the high positive charge on the metal. This maximizes the coordination number for the given metal in a high oxidation state.
 - **Ability to Form Multiple Bonds (Oxygen):** Oxygen, in particular, has the ability to form multiple bonds (double or triple bonds) with the metal, further strengthening the metal-ligand interaction and stabilizing the high oxidation state (e.g., in oxoanions like MnO_4^- , CrO_4^{2-}).
 - **Absence of Reducing Properties:** Fluorine and oxygen are the strongest oxidizing agents (fluorine is the strongest, oxygen is next). This means they are not easily oxidized themselves. In high oxidation states, the metal ions are strong oxidizing agents and would readily oxidize less electronegative (and thus more easily oxidizable) halogens like chlorine, bromine, or iodine. Thus, forming stable compounds with F or O prevents the reduction of the metal. For example, higher oxidation states of metals readily oxidize Cl^- to Cl_2 or Br^- to Br_2 .
- (b) Lanthanides predominantly exhibit a +3 oxidation state while actinides exhibit other than +3 oxidation states.
- **Reason:**
 - **Lanthanides (+3 Predominance):**
 - The distinguishing feature of lanthanides is the filling of the 4f orbitals. These 4f orbitals

are deeply buried within the atom, shielded effectively by the filled 5s and 5p orbitals.

- As a result, the 4f electrons are largely uninfluenced by the chemical environment and do not readily participate in bonding.
- The most stable oxidation state for almost all lanthanides is +3, formed by the loss of the two 6s electrons and one 4f electron (or one 5d electron if present, followed by one 4f electron). This leads to an f^n configuration which is relatively stable and explains the uniformity in their chemical behavior.
- While +2 and +4 states exist for some (e.g., Eu^{2+} , Yb^{2+} , Ce^{4+} , Tb^{4+}), these are less common and arise from achieving stable empty, half-filled, or fully-filled f-subshells (f^0 , f^7 , f^{14} configurations).

- **Actinides (Variable Oxidation States):**

- In actinides, the 5f orbitals are less effectively shielded than the 4f orbitals in lanthanides. They are more exposed to the environment and are closer in energy to the 6d and 7s orbitals.
- This allows the 5f electrons to participate more readily in bonding, along with the 6d and 7s electrons.
- Consequently, actinides exhibit a wider range of oxidation states beyond +3 (e.g., +4, +5, +6, +7). For instance, uranium, neptunium, and plutonium commonly show higher oxidation states. The +3 state is also common

but not as exclusively dominant as in lanthanides.

- (c) (i) Transition elements and their compounds act as good catalysts.

- **Reason:**

- **Variable Oxidation States:** Transition metals can readily switch between different oxidation states. This allows them to act as electron donors or acceptors in reaction mechanisms, forming unstable intermediates and regenerating themselves at the end of the catalytic cycle. This is crucial for redox reactions.
- **Large Surface Area (for heterogeneous catalysis):** Many transition metals and their compounds (especially oxides) can exist as fine powders or have porous structures, providing a large surface area for reactants to adsorb onto. This is vital for heterogeneous catalysis.
- **Formation of Intermediates with Reactants:** Transition metals can form temporary bonds with reactant molecules (adsorption) through their vacant d-orbitals. This adsorption often weakens bonds within the reactant molecules, making them more reactive.
- **Ability to Form Complex Intermediates:** The availability of vacant d-orbitals and variable oxidation states allows transition metals to form a variety of intermediate complexes with reactants, providing alternative reaction pathways with lower activation energies.

- **Defect Structures:** Many transition metal oxides and sulfides exhibit non-stoichiometric compositions and defect structures, which can provide active sites for catalytic reactions.
- (c) (ii) Absorption spectra of transition metal ions are broad.
 - **Reason:**
 - **d-d Transitions and Ligand Field Effects:** The absorption spectra of transition metal ions arise from electronic transitions between split d-orbitals (d-d transitions) under the influence of the ligand field.
 - **Vibrational Coupling:** When a transition metal complex absorbs light, not only does an electronic transition occur, but there are also simultaneous changes in the vibrational energy levels of the bonds within the complex. The electronic transitions are coupled with these vibrational transitions (vibronic coupling).
 - **Broadening Effect:** At room temperature, molecules exist in various vibrational energy states. When light is absorbed, an electron can be promoted from a ground electronic state (with various vibrational levels) to an excited electronic state (also with various vibrational levels). This results in a range of slightly different energy transitions, leading to a broadening of the absorption bands rather than sharp, discrete lines.
 - **Solvation and Temperature Effects:** Interactions with solvent molecules and temperature fluctuations also contribute to the broadening of the absorption

bands by affecting the exact energy levels and splitting patterns of the d-orbitals.

3. (a) (i) Write the number of unpaired electrons in Ce^{4+} (At. No.=58) and Eu^{3+} (At. No.=63).

○ **Cerium (Ce):** Atomic number 58.

- Electronic configuration: $[\text{Xe}] 4f^1 5d^1 6s^2$
- **Ce^{4+} :** Formed by losing all 4 valence electrons (one 4f, one 5d, two 6s).
- Configuration of Ce^{4+} : $[\text{Xe}] 4f^0$
- Number of unpaired electrons in Ce^{4+} : **0** (It has a stable noble gas configuration, making it diamagnetic).

○ **Europium (Eu):** Atomic number 63.

- Electronic configuration: $[\text{Xe}] 4f^7 6s^2$ (Europium is an exception and fills 4f half-shell for stability)
- **Eu^{3+} :** Formed by losing the two 6s electrons and one 4f electron.
- Configuration of Eu^{3+} : $[\text{Xe}] 4f^6$
- To find unpaired electrons in $4f^6$:
 - According to Hund's rule, electrons will singly occupy all orbitals before pairing.
 - f-subshell has 7 orbitals: $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow _$
 - Number of unpaired electrons in Eu^{3+} : **6**

○ **Answer:**

- Ce^{4+} : **0** unpaired electrons
- Eu^{3+} : **6** unpaired electrons

4. (b) Calculate the magnetic moment of Europium (III) ($L=3$). Explain the discrepancy between observed (3.4-3.6 BM) and calculated value.

• **Calculation of Magnetic Moment for Eu^{3+} :**

- For lanthanides, the magnetic moment is calculated using the total angular momentum quantum number (J), which accounts for both spin and orbital angular momentum coupling. The formula is:

- $\mu_J = g\sqrt{J(J+1)} \text{ BM (Bohr Magnetons)}$

- Where g is the Lande g -factor: $g = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)}$

- **For $\text{Eu}^{3+} (4f^6)$:**

- **Spin Multiplicity (S):**

- Number of unpaired electrons, $n = 6$.
- Total spin, $S = n/2 = 6/2 = 3$.

- **Orbital Angular Momentum (L):**

- The f -orbitals have m_l values: -3, -2, -1, 0, +1, +2, +3.
- For f^6 , the electrons are distributed:

- $\uparrow^{+3} \uparrow^{+2} \uparrow^{+1} \uparrow^0 \uparrow^{-1} \uparrow^{-2} \underline{\quad}^{-3}$

- $L = (+3) + (+2) + (+1) + (0) + (-1) + (-2) = +3$. So, $L = 3$.

- **Total Angular Momentum (J):**

- For an f -shell less than half-filled, $J = L - S$.
- For an f -shell more than half-filled, $J = L + S$.

- Since Eu^{3+} (f^6) is less than half-filled (f^7 is half-filled), $J = L - S$.

- $J = 3 - 3 = 0$.

▪ **Lande g-factor (g):**

- $$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$
- If $J = 0$, the denominator $2J(J + 1)$ becomes 0. This indicates that the formula for μ_J is not directly applicable when $J=0$.
- A state with $J=0$ means zero total angular momentum, implying zero magnetic moment.
- Therefore, the calculated magnetic moment using this formula would be $\mu_J = 0$.

• **Discrepancy between Observed (3.4-3.6 BM) and Calculated (0 BM) Value:**

- The discrepancy arises because the formula $\mu_J = g\sqrt{J(J + 1)}$ assumes that only the ground state contributes to the magnetic moment.
- For Eu^{3+} ($4f^6$), the ground state term symbol is 7F_0 (with $J=0$). According to this, the magnetic moment should be 0 BM.
- However, the $4f^6$ configuration has very closely spaced excited energy levels (specifically, the 7F_1 level is only about 300 cm^{-1} above the 7F_0 ground state).
- At ambient temperatures, there is significant **thermal population of these low-lying excited states**.
- These excited states have non-zero J values (e.g., 7F_1 has $J=1$), and thus they contribute significantly to the observed magnetic moment.

- Therefore, the observed magnetic moment of Eu^{3+} (3.4-3.6 BM) is a result of the contribution from these thermally populated excited states, not just the $J=0$ ground state. The formula's assumption of only ground state contribution breaks down due to the very small energy gap between the ground and first excited states.

3. (c) Explain (any one):

- (i) Micas are harder than clay.

▪ **Reason:**

- **Structure:** Both micas and clays are phyllosilicates (sheet silicates), meaning their basic structural unit is a tetrahedral layer of silicate (SiO_4) linked to an octahedral layer of metal hydroxides (e.g., $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$). However, their specific arrangements and bonding differ.
- **Micas:** Micas have a T-O-T (tetrahedral-octahedral-tetrahedral) layer structure, with a strong interlayer bonding. The negative charge on the silicate layers (due to isomorphic substitution of Si^{4+} by Al^{3+}) is balanced by large monovalent or divalent cations (like K^+ or Ca^{2+}) that are located between the T-O-T layers. These interlayer cations are strongly held within hexagonal rings of oxygen atoms and form strong electrostatic bonds, creating a rigid and strong layered structure. This strong interlayer binding makes micas hard and enables them to cleave into thin, flexible sheets.
- **Clays:** Clays, on the other hand, typically have T-O (tetrahedral-octahedral) or T-O-T structures with weaker interlayer forces. In many clays (e.g., kaolinite, a 1:1 clay), there is minimal or no

isomorphic substitution, and thus very little net negative charge on the layers. The layers are held together primarily by weaker forces like van der Waals forces and hydrogen bonding. In 2:1 clays (like montmorillonite), while there is some isomorphic substitution, the interlayer cations (often hydrated Na^+ or Ca^{2+}) are much more loosely held and can exchange easily. This allows for easier slippage and separation of layers, making clays much softer and exhibiting plasticity when wet.

- **Conclusion:** The presence of strong, fixed interlayer cations in micas, leading to strong electrostatic bonding between the layers, is the primary reason for their hardness compared to clays where interlayer bonding is weaker and layers can slide past each other more easily.
- (ii) Structure of cyclic phosphazene (trimer).
 - **Structure:**
 - The most common cyclic phosphazene trimer is **hexachlorocyclotriphosphazene**, $(\text{NPCl}_2)_3$.
 - It has a six-membered ring structure consisting of alternating phosphorus (P) and nitrogen (N) atoms.
 - Each phosphorus atom is bonded to two chlorine (Cl) atoms.
 - The ring is essentially planar or nearly planar.
 - The bonds within the ring (P-N bonds) exhibit a delocalized π system, similar to benzene, giving the ring unusual stability and aromatic-like properties. However, it's not a true aromatic system in the sense of benzene due to the involvement of d-

orbitals on phosphorus. The bonding is often described as π -delocalization involving the p-orbitals of nitrogen and the d-orbitals of phosphorus ($p\pi - d\pi$ bonding).

- The bond angles around nitrogen are approximately 120° , and around phosphorus, they are close to tetrahedral (depending on the substituents).
- The P-N bond lengths in the ring are intermediate between single and double bonds, indicating electron delocalization.

▪ **Drawing (Descriptive):**

- Imagine a hexagon.
- Alternate the vertices with P and N atoms.
- P-N-P-N-P-N in a ring.
- Each P atom has two Cl atoms attached to it, like this:
 - Cl
 - |
 - P -- N
 - || /
 - N -- P -- Cl
 - / ||
 - Cl -- P -- N
 - |
 - Cl

- (This is a simplified representation showing the connectivity. The actual bonding involves delocalized π electrons across the P-N bonds in the ring.)
4. (d) Advantages and disadvantages of digestion in gravimetric analysis.
- **Digestion in Gravimetric Analysis:** Digestion is a process where a precipitate is allowed to stand in contact with the mother liquor (the solution from which it precipitated) for a period, often at an elevated temperature. This process leads to improvements in the precipitate's properties.
 - **Advantages of Digestion:**
 - a. **Increased Particle Size (Crystal Growth):** Digestion promotes the growth of larger, more perfect crystals. Smaller crystals (often formed initially) tend to dissolve and recrystallize onto larger ones (Ostwald ripening). Larger crystals are easier to filter and wash, reducing losses.
 - b. **Improved Purity:** During recrystallization, impurities adsorbed on the surface of smaller crystals are released back into the solution. As larger, purer crystals form, they have a smaller surface area to volume ratio, leading to less adsorption of impurities. This results in a purer precipitate.
 - c. **Reduced Co-precipitation:** Digestion can minimize co-precipitation (the contamination of the desired precipitate by other soluble components from the solution). By allowing time for equilibrium to establish and for impurities to desorb, the precipitate becomes cleaner.
 - d. **Easier Filtration:** Larger particles formed during digestion tend to settle faster and are less likely to clog the filter pores, making filtration more efficient and faster.

- e. **Less Tendency for Peptization:** Digestion can make the precipitate less prone to peptization (the dispersion of a coagulated precipitate into a colloidal state upon washing, especially with pure water). Larger, denser particles are more stable and less likely to redisperse.
- **Disadvantages of Digestion:**
 - f. **Increased Analysis Time:** Digestion can be a time-consuming step, as it requires the precipitate to stand for several hours or even overnight. This extends the overall analysis time.
 - g. **Loss of Analyte due to Solubility:** If the precipitate has even a slight solubility in the mother liquor, prolonged digestion can lead to a measurable loss of the analyte into the solution, resulting in negative errors. This is particularly critical for precipitates with higher solubilities.
 - h. **Hydrolysis or Decomposition:** Some precipitates might undergo hydrolysis or decomposition if digested for too long or at too high a temperature, leading to a change in stoichiometry or loss of the desired form.
 - i. **Contamination from Digestion Vessels:** Prolonged digestion, especially at elevated temperatures, might lead to leaching of impurities from the glassware or containers into the solution, contaminating the precipitate.
 - j. **Possible Co-precipitation of Other Species:** In some cases, prolonged digestion might actually lead to the co-precipitation of other species that were initially soluble but become less soluble over time or at elevated temperatures.
4. (a) Given below are the Latimer diagrams of Mn (Reduction potential, E° in Volt) in acidic medium and basic medium: [followed by the diagrams] Answer the following questions with the help of above diagrams :

- (i) Write the balanced half reaction for the reduction of MnO_4^- to Mn^{2+} in acidic medium. Find the standard reduction potential for the reaction.
- **Latimer Diagram (Acidic Medium) for Mn:** ($\text{MnO}_4^- \xrightarrow{-0.564\text{V}} \text{MnO}_4^{2-} \xrightarrow{-2.26\text{V}} \text{MnO}_3^- \xrightarrow{-4.27\text{V}} \text{MnO}_2 \xrightarrow{-0.95\text{V}} \text{Mn}^{3+} \xrightarrow{-1.51\text{V}} \text{Mn}^{2+} \xrightarrow{-1.18\text{V}} \text{Mn}$)
- **Balanced Half-Reaction for MnO_4^- to Mn^{2+} (Acidic Medium):**
 - **Step 1: Balance Mn atoms:**
 - $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
 - **Step 2: Balance O atoms by adding H_2O :**
 - $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 - **Step 3: Balance H atoms by adding H^+ :**
 - $\text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 - **Step 4: Balance charges by adding electrons:**
 - Left side charge: $-1 + 8 = +7$
 - Right side charge: $+2 + 0 = +2$
 - To balance, add 5 electrons to the left side.
 - **$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$**
- **Standard Reduction Potential (E°):**
 - We need to calculate the overall E° for the multi-step reduction. We use the relationship $\Delta G^\circ = -nFE^\circ$, or for multiple steps, $nE^\circ = \sum n_i E_i^\circ$.
 - The steps involved from MnO_4^- to Mn^{2+} are:





- Total number of electrons transferred (n) = 1 + 1 + 1 + 1 + 1 = 5 e⁻.
- Overall $nE^\circ = n_1E_1^\circ + n_2E_2^\circ + n_3E_3^\circ + n_4E_4^\circ + n_5E_5^\circ$
- $5 \times E^\circ = (1 \times 0.564) + (1 \times 2.26) + (1 \times 4.27) + (1 \times 0.95) + (1 \times 1.51)$
- $5 \times E^\circ = 0.564 + 2.26 + 4.27 + 0.95 + 1.51$
- $5 \times E^\circ = 9.554$
- $E^\circ = \frac{9.554}{5}$
- $E^\circ = 1.9108 \text{ V}$

• **Answer:**

- Balanced Half-Reaction: **$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$**
- Standard Reduction Potential (E°): **1.91 V** (rounded to two decimal places)
- (ii) In which of the medium, acidic or basic Mn(III) is more stable? Justify your answer.

• **Stability of Mn(III):**

- To determine the stability of Mn(III) against disproportionation, we look at the reduction potentials involving Mn(III) in both diagrams. A species is unstable to disproportionation if the reduction potential to its lower oxidation state is higher than the

reduction potential from its higher oxidation state. Conversely, it is stable if the potentials indicate otherwise.

○ **In Acidic Medium (Latimer Diagram from above):**

- Reduction of Mn(III) to Mn(II): $\text{Mn}^{3+} \xrightarrow{1.51V} \text{Mn}^{2+}$
- Reduction of Mn(IV) to Mn(III): $\text{MnO}_2 \xrightarrow{0.95V} \text{Mn}^{3+}$
- Here, $E^\circ(\text{Mn}^{3+}/\text{Mn}^{2+}) = 1.51V$ and $E^\circ(\text{MnO}_2/\text{Mn}^{3+}) = 0.95V$.
- Since $1.51V > 0.95V$, Mn(III) in acidic medium has a greater tendency to be reduced to Mn(II) than to be formed from Mn(IV). This indicates that Mn(III) in acidic medium is **unstable to disproportionation**; it will disproportionate into Mn(II) and Mn(IV). ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{MnO}_2$).
- Alternatively, the E° to the left (reduction from higher oxidation state) is lower than the E° to the right (reduction to lower oxidation state), indicating instability.

○ **In Basic Medium (Assuming standard basic Latimer diagram values):**

- $(\text{MnO}_4^- \xrightarrow{-0.59V} \text{MnO}_4^{2-} \xrightarrow{-0.20V} \text{MnO}_2 \xrightarrow{-0.05V} \text{Mn(OH)}_3 \xrightarrow{-1.55V} \text{Mn(OH)}_2 \xrightarrow{-1.55V} \text{Mn})$
- Reduction of Mn(III) to Mn(II): $\text{Mn(OH)}_3 \xrightarrow{-1.55V} \text{Mn(OH)}_2$
- Reduction of Mn(IV) to Mn(III): $\text{MnO}_2 \xrightarrow{-0.05V} \text{Mn(OH)}_3$
- Here, $E^\circ(\text{Mn(OH)}_3/\text{Mn(OH)}_2) = -1.55V$ and $E^\circ(\text{MnO}_2/\text{Mn(OH)}_3) = -0.05V$.
- Since $-1.55V < -0.05V$, Mn(III) in basic medium has a lesser tendency to be reduced to Mn(II) than to be formed

from Mn(IV). This indicates that Mn(III) in basic medium is **stable to disproportionation**.

- **Answer:** Mn(III) is more stable in **basic medium**.
- **Justification:** In acidic medium, Mn(III) disproportionates because the potential for its reduction to Mn(II) (1.51 V) is higher than the potential for its formation from Mn(IV) (0.95 V). This means Mn(III) is a strong oxidizing agent and also a strong reducing agent in acidic solution. In basic medium, the potential for its reduction to Mn(II) (-1.55 V) is lower than the potential for its formation from Mn(IV) (-0.05 V), indicating that it is stable against disproportionation.
 - (iii) Using the given Latimer diagram for manganese in acidic medium, construct the Frost diagram to determine the most stable oxidation state of manganese. Explain your reasoning based on the diagram.
- **Construction of Frost Diagram for Mn in Acidic Medium:**
 - A Frost diagram plots nE° (where n is the oxidation state, and E° is the standard reduction potential from the highest oxidation state to that state, often referenced to the element in its standard state, Mn(0)) vs. the oxidation state (n).
 - The most stable oxidation state corresponds to the lowest point on the Frost diagram.
 - Disproportionation occurs if a species lies above the line connecting its adjacent oxidation states.
 - Values from the Latimer diagram (acidic):

$$\begin{array}{ccccccc} \text{MnO}_4^- (+7) & \xrightarrow{0.564V} & \text{MnO}_4^{2-} (+6) & \xrightarrow{2.26V} & \text{MnO}_3^- (+5) & \xrightarrow{4.27V} & \text{MnO}_2 (+4) \\ & & & & & & \xrightarrow{0.95V} & \text{Mn}^{3+} (+3) & \xrightarrow{1.51V} & \text{Mn}^{2+} (+2) & \xrightarrow{1.18V} & \text{Mn} (0) \end{array}$$
 - **Calculation of nE° for each oxidation state (referenced to Mn(0)):**

- **Mn(0):** (0, 0) - Origin point.
- **Mn(II) (Mn^{2+}):**
 - $E^\circ(Mn^{2+}/Mn) = 1.18V$
 - $nE^\circ = 2 \times 1.18 = 2.36$
 - Point: (2, 2.36)
- **Mn(III) (Mn^{3+}):**
 - Need E° from Mn(III) to Mn(0). This involves $Mn^{3+} \rightarrow Mn^{2+} \rightarrow Mn$.
 - $E^\circ_{Mn^{3+}/Mn} = \frac{(1 \times 1.51) + (2 \times 1.18)}{3} = \frac{1.51 + 2.36}{3} = \frac{3.87}{3} = 1.29V$
 - $nE^\circ = 3 \times 1.29 = 3.87$
 - Point: (3, 3.87)
- **Mn(IV) (MnO_2):**
 - Need E° from Mn(IV) to Mn(0). This involves $MnO_2 \rightarrow Mn^{3+} \rightarrow Mn^{2+} \rightarrow Mn$.
 - $E^\circ_{MnO_2/Mn} = \frac{(1 \times 0.95) + (1 \times 1.51) + (2 \times 1.18)}{4} = \frac{0.95 + 1.51 + 2.36}{4} = \frac{4.82}{4} = 1.205V$
 - $nE^\circ = 4 \times 1.205 = 4.82$
 - Point: (4, 4.82)
- **Mn(V) (MnO_3^-):**
 - Need E° from Mn(V) to Mn(0). This involves $MnO_3^- \rightarrow MnO_2 \rightarrow Mn^{3+} \rightarrow Mn^{2+} \rightarrow Mn$.

$$E^\circ_{MnO_3^-/Mn} = \frac{(1 \times 4.27) + (1 \times 0.95) + (1 \times 1.51) + (2 \times 1.18)}{5} = \frac{4.27 + 0.95 + 1.51 + 2.36}{5} = \frac{9.09}{5} = 1.818V$$

$$nE^\circ = 5 \times 1.818 = 9.09$$

$$\text{Point: (5, 9.09)}$$

▪ **Mn(VI) (MnO_4^{2-}):**

- Need E° from Mn(VI) to Mn(0). This involves $MnO_4^{2-} \rightarrow MnO_3^- \rightarrow MnO_2 \rightarrow Mn^{3+} \rightarrow Mn^{2+} \rightarrow Mn$.

$$E^\circ_{MnO_4^{2-}/Mn} = \frac{(1 \times 2.26) + (1 \times 4.27) + (1 \times 0.95) + (1 \times 1.51) + (2 \times 1.18)}{6} = \frac{2.26 + 4.27 + 0.95 + 1.51 + 2.36}{6} = \frac{11.35}{6} = 1.89V$$

$$nE^\circ = 6 \times 1.89 = 11.35$$

$$\text{Point: (6, 11.35)}$$

▪ **Mn(VII) (MnO_4^-):**

- Need E° from Mn(VII) to Mn(0). This involves $MnO_4^- \rightarrow MnO_4^{2-} \rightarrow \dots \rightarrow Mn$.

$$E^\circ_{MnO_4^-/Mn} = \frac{(1 \times 0.564) + (1 \times 2.26) + (1 \times 4.27) + (1 \times 0.95) + (1 \times 1.51) + (2 \times 1.18)}{7} = \frac{0.564 + 2.26 + 4.27 + 0.95 + 1.51 + 2.36}{7} = \frac{11.914}{7} = 1.702V$$

$$nE^\circ = 7 \times 1.702 = 11.914$$

$$\text{Point: (7, 11.914)}$$

• **Frost Diagram (Qualitative sketch - plot these points):**

- Plot the points: (0,0), (2, 2.36), (3, 3.87), (4, 4.82), (5, 9.09), (6, 11.35), (7, 11.914).

- Connect the points.
 - **Determination of Most Stable Oxidation State:**
 - The most stable oxidation state corresponds to the **lowest point** on the Frost diagram.
 - In the acidic medium Frost diagram for manganese, **Mn(II) (Mn²⁺)** at (2, 2.36) will be the lowest point.
 - **Reasoning:**
 - A species located at a "valley" or the lowest point in a Frost diagram is the most thermodynamically stable with respect to both oxidation and reduction. It indicates that reducing it to a lower oxidation state or oxidizing it to a higher oxidation state is unfavorable compared to other species.
 - In the acidic medium, Mn²⁺ is the most stable state, which is consistent with the general observation that manganese typically exists as Mn²⁺ in acidic solutions. Other higher oxidation states like Mn³⁺, Mn(IV), Mn(V), Mn(VI), and Mn(VII) are all unstable to disproportionation to some extent or are strong oxidizing agents that will reduce to Mn²⁺. For example, Mn³⁺ lies above the line connecting Mn²⁺ and MnO₂, indicating it disproportionates.
5. (b) (i) Explain the reason for the validity of spin only expression to calculate the magnetic moment for ions of first transition series.
- **Spin-Only Magnetic Moment Formula:** $\mu_s = \sqrt{n(n + 2)}$ BM, where n is the number of unpaired electrons.
 - **Reason for Validity in First Transition Series:**
 - The spin-only formula assumes that the observed magnetic moment arises solely from the spin angular momentum of the unpaired electrons and that the contribution from orbital angular momentum is negligible or "quenched".

- **Quenching of Orbital Angular Momentum:** In ions of the first transition series (3d series), the 3d orbitals are the outermost orbitals (or at least less shielded than 4f). When these ions are surrounded by ligands in a complex (which is typically the case in solutions or solids), the electric field created by the ligands (the crystal field or ligand field) interacts strongly with the d-orbitals.
- This strong interaction restricts the free movement (orbital motion) of the electrons within these d-orbitals. The orbital degeneracy of the d-orbitals is lifted, and their shapes are significantly influenced by the ligand field.
- This interaction effectively "quenches" or removes the contribution of the orbital angular momentum to the total magnetic moment. The electrons are essentially "fixed" in specific spatial orientations by the ligand field, preventing their free circulation.
- **Dominant Spin Contribution:** As a result, the observed magnetic moment is almost entirely due to the spin of the unpaired electrons.
- **Exceptions:** Orbital contribution is not entirely quenched in some specific cases, particularly for ions with certain d-electron configurations (e.g., d^1, d^2, d^6, d^7 in octahedral fields, or in tetrahedral fields) where there is residual orbital angular momentum, leading to higher observed magnetic moments than predicted by the spin-only formula. However, for most common complexes of the first transition series, especially those with an A or E ground state term (which corresponds to non-degenerate or doubly degenerate orbital states), the quenching is nearly complete, and the spin-only formula provides a good approximation.

- (ii) A M^{2+} ion of first transition series has been observed to have four unpaired electrons. Calculate its magnetic moment using spin-only formula,

- **Calculation:**

- Given: M^{2+} ion of first transition series.
- Number of unpaired electrons (n) = 4.
- Spin-only magnetic moment formula: $\mu_s = \sqrt{n(n+2)} \text{ BM}$
- Substitute $n = 4$:
 - $\mu_s = \sqrt{4(4+2)} \text{ BM}$
 - $\mu_s = \sqrt{4(6)} \text{ BM}$
 - $\mu_s = \sqrt{24} \text{ BM}$
 - $\mu_s \approx 4.8989... \text{ BM}$

- **Answer:** The magnetic moment of the M^{2+} ion is approximately **4.90 BM**.

- (iii) What is the effect of curie temperature in ferromagnetism?

- **Curie Temperature (T_c) and Ferromagnetism:**

- **Definition:** The Curie temperature (or Curie point) is a critical temperature for ferromagnetic materials. It is the temperature above which a ferromagnetic material loses its strong ferromagnetic properties and becomes paramagnetic.
- **Effect:**
 - **Below T_c (Ferromagnetic State):** In a ferromagnetic material below its Curie temperature, the magnetic moments of individual atoms or ions are spontaneously aligned parallel to each other within macroscopic regions

called **magnetic domains**. This strong alignment occurs due to strong exchange interactions between neighboring atoms. This results in a large net magnetization even in the absence of an external magnetic field.

- **At and Above T_C (Paramagnetic State):** As the temperature of a ferromagnetic material increases and reaches the Curie temperature, the thermal energy of the atoms becomes sufficient to overcome the strong exchange interactions that cause the spontaneous alignment of magnetic moments. The thermal agitation disrupts the ordered alignment within the domains.
- Above T_C , the material loses its permanent magnetism. The domains are destroyed, and the magnetic moments become randomly oriented. The material then behaves like a paramagnetic substance, meaning it only exhibits weak magnetism when placed in an external magnetic field (due to the alignment of individual moments with the field, which disappears once the field is removed).
- **In Summary:** The Curie temperature marks the transition point where the ordered, spontaneously magnetized state of a ferromagnet is destroyed by thermal disorder, leading to a paramagnetic state.

5. (a) (i) Write a short note on borates.

- **Borates:**
 - **Definition:** Borates are compounds containing boron and oxygen, often with other elements, derived from boric acid (H_3BO_3) or its polymeric forms. They are characterized by the presence of trigonal planar BO_3 units and/or tetrahedral BO_4 units.
 - **Structure:** The fundamental building blocks of borates are BO_3 triangles and BO_4 tetrahedra. These units can link together in

various ways (sharing oxygen atoms) to form a wide range of structures, including:

- **Isolated units:** Like in orthoborates (BO_3^{3-}).
 - **Chain structures:** Where BO_3 or BO_4 units link to form linear or branched chains.
 - **Ring structures:** Common in metaborates (e.g., cyclic trimers ($B_3O_6^{3-}$), often found as $(BO_2)_n$).
 - **Layer structures:** Resembling silicates, where layers of boron-oxygen polyhedra are formed.
 - **Framework structures:** More complex 3D networks.
- **Examples:**
- **Borax (Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$):** A common borate mineral, containing a complex polyanion ($[B_4O_5(OH)_4]^{2-}$).
 - **Boric acid (H_3BO_3):** A weak acid, which is essentially a layered polymer in solid form.
 - **Boron nitride (BN):** Although not strictly a borate (no oxygen), it shares structural similarities to carbon allotropes (graphite-like and diamond-like forms) and is often discussed alongside boron compounds.
- **Properties and Uses:**
- **Glass and Ceramics:** Borates are widely used in the production of borosilicate glass (e.g., Pyrex) due to their low coefficient of thermal expansion and good heat resistance. They are also used as fluxes in ceramics and glazes.

- **Detergents and Cleaning Agents:** Borax is a common ingredient in laundry detergents and household cleaners due to its buffering properties and ability to soften water.
 - **Flame Retardants:** Borates are effective flame retardants for wood and cellulosic materials.
 - **Agriculture:** Used as micronutrients (boron) in fertilizers for plants.
 - **Pesticides:** Boric acid is used as an insecticide.
 - **Medicine:** Boric acid has antiseptic properties.
 - **Nuclear Industry:** Boron (specifically ^{10}B isotope) is an excellent neutron absorber, used in nuclear reactors for control rods and shielding.
- (ii) Discuss the primary differences in the general properties of inorganic and organic polymers (any three).

- **Primary Differences in General Properties:**

- k. **Backbone Composition:**

- **Organic Polymers:** Typically have a backbone composed primarily of carbon atoms, often with hydrogen, oxygen, nitrogen, or sulfur atoms attached. Examples: polyethylene (C-C-C-C backbone), nylon (C-C-N-C-C-N backbone).
 - **Inorganic Polymers:** Have a backbone that does not rely on carbon atoms. Instead, they typically contain other elements like silicon, phosphorus, sulfur, boron, nitrogen, oxygen, or metals, often in repeating units. Examples: silicones (-Si-O-Si-O- backbone), polyphosphazenes (-P=N-P=N- backbone), polysulfanes (-S-S-S-S- backbone).

- l. **Thermal Stability:**

- **Organic Polymers:** Generally have lower thermal stability. Many start to soften, melt, or decompose at relatively low temperatures (e.g., below 200-300°C), due to the lower bond energies of C-C and C-H bonds compared to many inorganic bonds, and their susceptibility to oxidation.
- **Inorganic Polymers:** Often exhibit significantly higher thermal stability. Their backbones frequently involve strong, stable bonds (e.g., Si-O, P=N, B-N) that are less susceptible to thermal degradation. Many inorganic polymers can withstand temperatures exceeding 300°C, and some even up to 1000°C or more.

m. **Chemical and Oxidative Stability:**

- **Organic Polymers:** Can be susceptible to degradation by UV radiation, strong acids/bases, and oxidation (especially those with unsaturated bonds or easily oxidizable groups). Many are flammable.
 - **Inorganic Polymers:** Tend to have higher chemical and oxidative stability. For example, silicones are highly resistant to oxidation, UV radiation, and many chemical reagents. Polyphosphazenes can be designed to be highly flame-retardant and resistant to various chemicals. This makes them suitable for harsh environments.
- **Other Differences (Could also be chosen):**
- **Flexibility/Elasticity:** Many organic polymers are flexible and elastic (rubbers, plastics). Inorganic polymers can range from flexible (silicones) to rigid (some phosphazenes, ceramics).
 - **Electrical Conductivity:** Most organic polymers are electrical insulators. Some inorganic polymers can be

conductive (e.g., certain polysulfur nitrides) or semiconductors.

- **Applications:** Organic polymers are ubiquitous in everyday items (packaging, textiles, building materials). Inorganic polymers find niche applications in high-performance materials, aerospace, electronics, and biomedicine due to their unique properties.

6. (b) (i) What is the structural difference between pyroxenes and amphiboles?

- **Both Pyroxenes and Amphiboles are important classes of inosilicates (chain silicates).** Their primary structural difference lies in the type of silicate chain they form.

- **Pyroxenes (Single-Chain Silicates):**

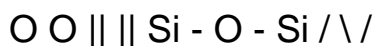
- **Structure:** Pyroxenes are built from **single chains** of silicate tetrahedra.
- **Tetrahedra Linkage:** Each SiO_4 tetrahedron shares two oxygen atoms with adjacent tetrahedra, forming a continuous chain.
- **Repeat Unit:** The fundamental repeat unit in the chain is SiO_3^{2-} .
- **Formula:** General formula is often represented as $MSiO_3$ or $M_2Si_2O_6$, where M represents various metal cations (e.g., Mg^{2+} , Fe^{2+} , Ca^{2+} , Na^+ , Al^{3+}).
- **Properties:** Tend to be more dense and harder than amphiboles, with cleavage angles around 90° .
- **Example:** Enstatite ($MgSiO_3$), Diopside ($CaMgSi_2O_6$).

- **Amphiboles (Double-Chain Silicates):**

- **Structure:** Amphiboles are characterized by **double chains** of silicate tetrahedra.

- **Tetrahedra Linkage:** These double chains are formed by two single chains linked together by sharing oxygen atoms. Specifically, half of the SiO_4 tetrahedra in each chain share three oxygen atoms (two within their own chain and one with the adjacent chain), while the other half share two oxygen atoms within their own chain.
- **Repeat Unit:** The fundamental repeat unit in the double chain is $Si_4O_{11}^{6-}$.
- **Formula:** General formula is complex, often written as $A_0 - 1B_2C_5T_8O_{22}(OH, F, Cl)_2$, where T is typically Si or Al, and A, B, C are various metal cations. A simpler representation is $M_7Si_8O_{22}(OH)_2$.
- **Properties:** Generally less dense and softer than pyroxenes, with characteristic cleavage angles of about 56° and 124° . They also contain hydroxyl groups (OH) within their structure, which are absent in pyroxenes.
- **Example:** Tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$), Hornblende.
- **Summary:** The core difference is the polymerization of silicate tetrahedra: **pyroxenes have single, unbranched chains, while amphiboles have wider, ladder-like double chains.** This structural difference leads to distinct physical and chemical properties.
 - (ii) Draw the structures of following ions : $Si_2O_7^{2-}$, $Si_3O_6^{6-}$
- **Structures of Ions:**
 - **$Si_2O_7^{6-}$ (Disilicate ion / Pyro-silicate ion):**
 - **Description:** This ion consists of two SiO_4 tetrahedra linked together by sharing one common oxygen atom. The two silicon atoms are bridged by a single oxygen atom.
 - **Drawing (Conceptual):**

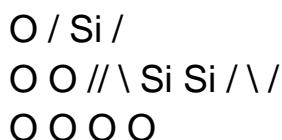
- Two silicon atoms (Si) are central.
- Each Si is bonded to 4 oxygen atoms.
- One oxygen atom is shared between the two Si atoms (bridging oxygen).
- The remaining 6 oxygen atoms are terminal (each bonded to only one Si).
- The overall charge is -6.



O O O O Charge: The six terminal oxygens each have a -1 charge, and the bridging oxygen has 0 charge (effectively sharing two bonds). So, 6 negative charges overall.

○ **$\text{Si}_3\text{O}_6^{6-}$ (Cyclic Trisilicate ion):**

- **Description:** This ion forms a three-membered ring structure consisting of three SiO_4 tetrahedra. Each silicon atom shares two oxygen atoms, forming a ring. This means each SiO_4 unit contributes an SiO_2 unit to the ring structure.
- **Drawing (Conceptual):**
 - Three silicon atoms (Si) and three oxygen atoms (O) form an alternating six-membered ring (Si-O-Si-O-Si-O).
 - Each Si atom in the ring is also bonded to two additional terminal oxygen atoms (which carry the negative charge).



- The simplified drawing of the ring is:
 - Si - O
 - ||
 - O - Si
 - ||
 - Si - O
 - Each Si in the ring has two additional terminal oxygens, each carrying a -1 charge. So, $3 \times 2 = 6$ negative charges overall.

6. (c) (i) Mention the criteria while selecting a wash solution in the gravimetric analysis.

- **Criteria for Selecting a Wash Solution in Gravimetric Analysis:**

- n. **Minimizing Loss of Analyte (Common Ion Effect):**

- The wash solution should contain an ion common to the precipitate. This is the most crucial criterion. According to the common ion effect, the solubility of the precipitate is significantly reduced when a soluble salt containing a common ion is present in the wash solution. This minimizes the dissolution of the precipitate during washing.
 - Example: For washing AgCl precipitate, a dilute solution of HNO_3 or $AgNO_3$ is preferred over pure water.

- o. **Removing Impurities Effectively:**

- The wash solution should be able to dissolve and remove adsorbed impurities from the surface of the precipitate.
 - However, it should not dissolve the precipitate itself.

p. Preventing Peptization:

- The wash solution should prevent peptization, which is the dispersion of the coagulated precipitate into a colloidal state upon washing, especially with pure water.
- Electrolytes in the wash solution (like those used for the common ion effect) help maintain the ionic strength and prevent the repulsive forces between precipitate particles from causing redispersion.

q. No Interference with Subsequent Steps:

- The wash solution should be volatile or easily removable upon drying/ignition of the precipitate. It should not leave behind any non-volatile residues that would add to the weight of the precipitate.
- It should not react with the precipitate or contaminate it.

r. Low Solubility of Precipitate in the Wash Solution:

- The chosen solvent for the wash solution should have a very low dissolving power for the precipitate. Often, a mixed solvent (e.g., water-alcohol) is used to decrease the solubility of the precipitate if it has some solubility in water.

s. Accessibility and Cost:

- The wash solution should be readily available and not excessively expensive.
- (ii) Which is more effective for washing a precipitate in the gravimetric analysis: using two portions of 50 mL or ten portions of 10 mL of each? Justify your answer.
- **More Effective Method:** Using **ten portions of 10 mL each** is more effective for washing a precipitate.

- **Justification:**

- **Principle:** The effectiveness of washing depends on the efficiency of removing impurities from the surface of the precipitate. Each time a fresh portion of wash solution is applied, it dilutes the concentration of impurities in the liquid adhering to the precipitate and removes a fraction of them.
- **Multiple Small Portions vs. Fewer Large Portions:**
 - When a precipitate is washed with multiple small portions, each successive portion of fresh wash solution removes a larger *proportion* of the remaining impurities compared to using a few large portions.
 - Although the total volume of wash solution is the same in both scenarios (100 mL), distributing it into more, smaller aliquots means that the concentration of impurities in the liquid surrounding the precipitate is repeatedly lowered to a greater extent.
 - Consider the impurities distributed between the precipitate surface and the wash liquid. Each washing step establishes a new equilibrium or approximation to it. The more times fresh, pure wash solution comes into contact with the precipitate, the more effectively the impurities are leached out.
- **Analogy:** Imagine trying to dilute a highly concentrated liquid by adding water. If you add all the water at once, you get one dilution. If you add the same total amount of water in several smaller increments, each time pouring off the diluted liquid and adding fresh water, you achieve a much greater overall dilution.
- **Mathematical Basis (simplified):** If C_0 is the initial concentration of impurity in the solution adhered to the precipitate, and 'V' is the volume of the adhered liquid, and 'v' is the volume of each wash portion, then the amount of impurity

removed is approximately proportional to 'v'. After 'n' washes, the remaining impurity is roughly proportional to $(V/(V + v))^n$. For a fixed total volume, increasing 'n' (number of portions) and decreasing 'v' (volume per portion) leads to a lower final concentration of impurity.

- **Conclusion:** Washing with multiple smaller portions is always more efficient than washing with fewer larger portions, even if the total volume of wash solution is the same.

7. (a) (i) What are silicones? What are the chain building and chain stopping units in silicones?

- **Silicones:**

- **Definition:** Silicones (more accurately, polysiloxanes) are a class of synthetic inorganic polymers that are characterized by a flexible backbone of alternating silicon and oxygen atoms (-Si-O-Si-O-), with organic groups (like methyl, ethyl, phenyl, etc.) attached to the silicon atoms.
- **General Formula:** $(R_2SiO)_n$, where R represents an organic group.
- **Properties:** Silicones exhibit a unique combination of properties, including:
 - High thermal stability (resistant to high and low temperatures).
 - Excellent chemical inertness (resistant to oxidation, UV radiation, and many chemicals).
 - Hydrophobicity (water repellent).
 - Good electrical insulation properties.
 - Low surface tension.
 - Non-toxic and biocompatible.

- **Applications:** Due to these properties, silicones are widely used in sealants, adhesives, lubricants, medical implants, cosmetics, cooking utensils, and electrical insulation.
- **Chain Building and Chain Stopping Units in Silicones:**
 - Silicones are typically synthesized by the hydrolysis and condensation of organochlorosilanes (R_nSiCl_{4-n}). The functionality (number of hydrolyzable groups) of the starting silane determines its role in polymer formation.
 - **Chain Building Units (D-units - D for Di-functional):**
 - **Chemical Formula:** (R_2SiO) (a repeating unit in the chain)
 - **Source:** Derived from **dialkyldichlorosilanes** (R_2SiCl_2).
 - **Function:** When R_2SiCl_2 is hydrolyzed, it forms $R_2Si(OH)_2$. These dihydroxy compounds can condense with other $R_2Si(OH)_2$ units or with chain-stopping units by forming -Si-O-Si- linkages, thereby **extending the polymer chain**. Each such unit forms two bonds within the polymer backbone.
 - Example: Dimethyldichlorosilane ($(CH_3)_2SiCl_2$) is a common precursor for linear silicone polymers.
 - **Chain Stopping Units (M-units - M for Mono-functional):**
 - **Chemical Formula:** $R_3SiO_{1/2}$ (effectively an end group)
 - **Source:** Derived from **trialkyldichlorosilanes** (R_3SiCl).
 - **Function:** When R_3SiCl is hydrolyzed, it forms R_3SiOH . This monohydroxy compound can condense with a chain-building unit, but it has only one reactive -OH group. Once it forms an -Si-O- bond with another unit, it has no further reactive sites to extend the chain. Thus, it acts as an **end**

cap, stopping the polymerization at that point and controlling the molecular weight of the polymer.

- Example: Trimethylchlorosilane ($(CH_3)_3SiCl$) is used to control the chain length of dimethicone.

8. (a) (ii) Identify the industries from the following which use silicones:
Rubber, Glass, Oil, Cement

- **Industries that use Silicones:**

- **Rubber:** Yes, silicones are used extensively in the rubber industry to produce silicone rubbers (elastomers) which have excellent heat resistance, flexibility at low temperatures, and chemical inertness, making them suitable for seals, gaskets, and medical devices.
- **Glass:** Yes, silicones are used in the glass industry as sealants, adhesives (e.g., for bonding glass in aquariums or windows), and coatings to impart water repellency or anti-scratch properties.
- **Oil:** Yes, silicones are used in the oil and gas industry as defoamers (to prevent foam formation in drilling fluids and petroleum processing), lubricants (silicone oils have high thermal stability), and in various sealing applications.
- **Cement:** Yes, silicones can be used in the cement industry as water repellents for concrete and masonry, as admixtures to improve workability and durability, and as sealants for construction joints.

- **Answer:** All the mentioned industries – **Rubber, Glass, Oil, and Cement** – use silicones.

9. (b) Match the uses with the polymers:

- **Gemstones with montmorillonites:**

- **Incorrect.** Montmorillonites are a type of clay mineral, primarily used in drilling fluids, absorbents, and as a component in some cosmetics. Gemstones are typically crystalline minerals like quartz, sapphire, emerald, etc.
- **Correct Match (Implicit for Gemstones):** Not directly provided, but natural gemstones are typically silicates, oxides, or other crystalline compounds.
- **Textiles with orthosilicates:**
 - **Incorrect.** Orthosilicates (SiO_4^{4-} units) are discrete tetrahedral units found in minerals like olivine. They are not polymeric and are not used in textiles. Textiles are made from fibers, which are organic polymers (e.g., cotton, wool, nylon, polyester) or sometimes inorganic fibers like fiberglass.
 - **Correct Match (for Textiles):** Organic polymers like Nylon, Polyester, Cotton, Wool.
- **Fertilizers with polyphosphazenes:**
 - **Incorrect.** Polyphosphazenes are a class of inorganic polymers known for their diverse properties (flame retardancy, biocompatibility, high temperature resistance) and niche applications in advanced materials, biomedicine, and aerospace. They are not typically used as fertilizers. Fertilizers commonly contain nitrogen, phosphorus, and potassium compounds.
 - **Correct Match (for Fertilizers):** Phosphate salts (e.g., ammonium phosphate), urea, potassium salts.
- **Paints with phosphates:**
 - **Correct.** Phosphates are indeed used in paints. For example, zinc phosphate is commonly used as a corrosion-inhibiting pigment in primers for metals. Other phosphate compounds can

act as dispersants, binders, or flame retardants in paint formulations.

- **Corrosion protection with Borates:**

- **Correct.** Borates are widely used for corrosion protection. For example, sodium borate (borax) is used as a corrosion inhibitor in cooling systems, antifreeze solutions, and metalworking fluids. They form a protective film on metal surfaces, preventing oxidation.

- **Matched Pairs (based on correctness):**

- **Paints with Phosphates**
- **Corrosion protection with Borates**

(The other given matches are incorrect based on standard uses.)

10. (c) Write short note on any one of the following:

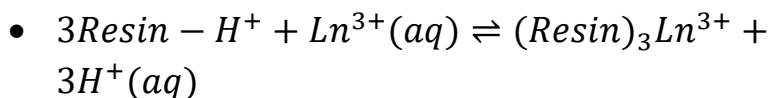
- (i) Ion exchange method for separation of lanthanides
- (ii) Lanthanide contraction and its consequences

- **(i) Ion Exchange Method for Separation of Lanthanides:**

- **Principle:** The ion exchange method is a highly effective and widely used technique for the separation and purification of individual lanthanide elements from their mixtures. It relies on the subtle differences in the hydrated ionic radii and complexing abilities of the trivalent lanthanide ions (Ln^{3+}).
- **Mechanism:**
 - i. **Ion Exchange Resin:** A column packed with a cation exchange resin is used. This resin consists of an insoluble polymer matrix containing acidic functional groups (e.g., sulfonic acid groups, $-\text{SO}_3\text{H}$), which are

typically in their protonated form or as sodium/ammonium salts (e.g., $\text{Resin} - \text{H}^+$ or $\text{Resin} - \text{NH}_4^+$).

- ii. **Loading:** The mixture of lanthanide ions (in solution) is passed through the column. The Ln^{3+} ions displace the H^+ or NH_4^+ ions from the resin, becoming adsorbed onto the resin.



- iii. **Elution with Complexing Agent:** A chelating agent (complexing agent) such as citric acid, α -hydroxyisobutyric acid, or EDTA, usually in a buffered solution, is then passed through the column.

- The lanthanide ions form stable complexes with the chelating agent. The stability of these complexes varies slightly across the lanthanide series due to the subtle decrease in ionic radius (lanthanide contraction).
- **Effect of Lanthanide Contraction:** As the ionic radius decreases across the series from La^{3+} to Lu^{3+} , the tendency to form complexes with the chelating agent slightly increases (smaller ions generally form more stable complexes with a given ligand due to higher charge density).
- Therefore, the **heavier lanthanides (smaller ions)**, which form slightly more stable complexes with the chelating agent, are released from the resin first (eluted first). They spend less time bound to the resin and more time in the mobile complexed form.

- Conversely, the **lighter lanthanides (larger ions)** form slightly weaker complexes and are retained more strongly by the resin, being eluted later.

iv. **Collection:** The eluent is collected in fractions, and each fraction is analyzed to identify the separated lanthanide.

- **Advantages:** This method allows for the separation of even very similar lanthanides, leading to high purity. It is relatively simple and efficient for laboratory-scale separations.

- **(ii) Lanthanide Contraction and its Consequences:**

- **Lanthanide Contraction Definition:**

- Lanthanide contraction refers to the steady and significant decrease in the atomic and ionic radii of the trivalent lanthanide ions (Ln^{3+}) as one proceeds across the lanthanide series from Lanthanum (La, At. No. 57) to Lutetium (Lu, At. No. 71).
- This contraction occurs because the 4f electrons, which are added sequentially across the series, provide very poor shielding of the nuclear charge. As a result, the effective nuclear charge experienced by the outermost 5s, 5p, and 6s electrons increases progressively, pulling these electrons closer to the nucleus and causing a contraction in atomic and ionic size.

- **Consequences of Lanthanide Contraction:**

v. **Similarity in Atomic/Ionic Radii of 2nd and 3rd Transition Series Elements:**

- The most significant consequence is that elements of the second transition series (e.g., Zr, Nb) have atomic and ionic radii very similar to their heavier counterparts in the third transition series (e.g., Hf, Ta).

- Normally, one would expect a significant increase in size down a group. However, the lanthanide contraction largely offsets the expected increase in size from the 2nd to the 3rd transition series.
- This similarity in size leads to remarkable similarities in chemical properties between the corresponding elements of the 2nd and 3rd transition series (e.g., Zr and Hf behave almost identically chemically), making their separation challenging.

vi. Increased Ionization Energies for 3rd Transition Series Elements:

- Due to the smaller size and increased effective nuclear charge, the electrons in the third transition series elements are held more tightly. This results in higher ionization energies for the 3rd transition series elements compared to the 2nd transition series, despite being in the same group.

vii. Increased Electronegativity:

- The increased effective nuclear charge also leads to a slight increase in the electronegativity of the elements of the third transition series.

viii. Higher Density of 3rd Transition Series Elements:

- Because the atomic mass increases significantly from the 2nd to 3rd transition series, but the atomic volume (due to similar radii) does not increase proportionally, the elements of the third transition series tend to have much higher densities than their counterparts in the second series.

ix. Effect on Basic Strength of Lanthanide Hydroxides:

- As the Ln^{3+} ionic radius decreases across the series, the charge density increases. This leads to a stronger attraction for hydroxide ions and a greater tendency for the Ln^{3+} ion to polarize the O-H bond in water. Consequently, the basic strength of the lanthanide hydroxides ($\text{Ln}(\text{OH})_3$) decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.

x. Effect on Complex Formation Tendency:

- The decreasing ionic size across the series (due to lanthanide contraction) leads to a gradual increase in the tendency of Ln^{3+} ions to form complexes with a given ligand, especially for those ligands that form coordinate bonds. This property is crucial for the separation of lanthanides by ion-exchange chromatography.