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d-Block Elements

Definition and Position

d-block elements are those elements in which the last electron enters the d-sub-shell of the penultimate shell. They are located in the middle of the periodic table, spanning groups 3 to 12.

Penultimate Shell

The penultimate shell is the shell just inside the valence shell. If the valence shell is the nth shell, the penultimate shell is the (n-1)th shell.

Transition Elements

Transition elements are d-block elements that have incompletely filled d-orbitals in their ground state or common oxidation states. They exhibit properties transitional between s-block and p-block elements.

Series of Transition Elements

- First transition series: 3d orbitals, Sc (21) to Zn (30)
- Second transition series: 4d orbitals, Y (39) to Cd (48)
- Third transition series: 5d orbitals, La (57) and Hf (72) to Hg (80)
- Fourth transition series: 6d orbitals, Actinium (89) and Rf (104) onwards (incomplete)

General Electronic Configuration

The valence shell electronic configuration of transition elements is $(n-1)d^{1-10}\ ns^{1-2}$, where n is the outermost shell.

Physical Properties

- All are metals, malleable and ductile except mercury (liquid)
- High thermal and electrical conductivity
- Metallic lustre and sonorous
- Atomic radii smaller than s-block but larger than p-block elements in the same period
- Lanthanide contraction causes 4d and 5d elements to have similar sizes
- Ionic radii decrease with increasing oxidation state
- Density increases from left to right in a period
- Ionisation enthalpy generally increases across the series with some irregularities
- Strong metallic bonding due to delocalised d-electrons
- High enthalpy of atomisation
- Variable oxidation states due to similar energies of ns and (n-1)d electrons
- Lower and irregular electrode potentials
- Catalytic properties due to multiple oxidation states and large surface area
- Magnetic properties: diamagnetic if all electrons paired, paramagnetic if unpaired electrons present
- High melting and boiling points except Zn, Cd, Hg
- Tendency to form complex ions
- Formation of coloured compounds due to d–d electronic transitions
- Formation of alloys due to similar atomic sizes and bonding
- Formation of interstitial compounds with small atoms like H, B, C, N

Chemical Properties

Transition metals form oxides with varying oxidation states and chemical nature (basic, amphoteric, acidic). They also form important compounds like potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$) with characteristic preparation methods, properties, and uses.

Solved Examples

Example 1

Given the standard electrode potentials (E°) for $Cr^{2+}/Cr = -0.9$ V, $Cr^{3+}/Cr^{2+} = -0.4$ V, $Mn^{2+}/Mn = -1.2$ V, $Mn^{3+}/Mn^{2+} = +1.5$ V, $Fe^{2+}/Fe = -0.4$ V, $Fe^{3+}/Fe^{2+} = +0.8$ V, comment on:

(a) Stability of Fe^{3+} compared to Cr^{3+} and Mn^{3+} in acid solution.

(b) Ease of oxidation of iron compared to chromium and manganese.

Solution:

(a) Cr^{3+} has a negative reduction potential, indicating it is stable and not easily reduced. Mn^{3+} has a large positive E°, so it is easily reduced to Mn^{2+} and is less stable. Fe^{3+} has a positive but smaller E° than Mn^{3+}, so its stability is intermediate.

(b) Mn^{2+} has the most negative reduction potential, meaning it is most easily oxidised. The order of ease of oxidation is Mn > Cr > Fe.

Example 2

Interpret the magnetic moment of the complex $K_4[Mn(CN)_6]$ with a magnetic moment of 2.2 BM.

Solution:

Mn is in +2 oxidation state. The magnetic moment of 2.2 BM indicates one unpaired electron, suggesting a low-spin complex with d^2sp^3 hybridisation due to the strong field ligand CN^-, resulting in an octahedral geometry.

Practice Set

- **Level 1 (Easy):** Define transition elements and state their general electronic configuration.
- **Level 2 (Moderate):** Explain why transition metals exhibit variable oxidation states.
- **Level 3 (Challenging):** Write the balanced chemical equation for the preparation of potassium dichromate from chromite ore.

Answer Key

- **Level 1:** Transition elements are d-block elements with incompletely filled d-orbitals. General electronic configuration: $(n-1)d^{1-10}\ ns^{1-2}$.
- **Level 2:** Variable oxidation states arise because ns and (n-1)d electrons have similar energies and can be lost during reactions.
- **Level 3:** $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$

f-Block Elements

Definition and Position

f-block elements are those in which electrons fill the (n-2)f sub-shell, the third shell from the outermost. They include two series: lanthanoids and actinoids, also called inner transition elements.

General Electronic Configuration

$(n-2)f^{1-14}$ $(n-1)d^{0-1}$ ns^2, with n=6 for lanthanoids and n=7 for actinoids. Exceptions exist.

Lanthanoids

Elements from Ce (Z=58) to Lu (Z=71) filling 4f orbitals.

Physical Properties

- Dense, soft, malleable, ductile metals
- High melting points
- Form alloys easily
- Magnetic properties: La^{3+} and Lu^{3+} are diamagnetic; others paramagnetic due to unpaired electrons
- Atomic and ionic radii decrease slightly across the series due to lanthanoid contraction

Chemical Properties

Highly electropositive metals with similar reactivity. Mainly +3 oxidation state, some +2 and +4. Some trivalent ions are coloured due to f–f electronic transitions.

Lanthanide Contraction

Steady decrease in size across lanthanoids due to poor shielding by 4f electrons, causing similar properties and difficulty in separation.

Uses

- Misch metal (alloy of cerium and other lanthanoids) used in lighter flints
- Lanthanoid oxides for glass polishing
- Cerium salts in dyeing and catalysis
- Catalysts in hydrogenation, dehydrogenation, petroleum cracking
- Pyrophoric alloys for tracer bullets and shells

Actinoids

Elements from Ac (Z=89) to Lr (Z=103) filling 5f orbitals. Elements beyond uranium are man-made and radioactive.

Physical Properties

- Dense, silvery white metals
- Highly electropositive
- High melting points
- Atomic and ionic radii decrease across series due to actinoid contraction
- Many are coloured and paramagnetic

Chemical Properties

Less reactive towards acids, common oxidation state +3, also +4 to +7. Many are radioactive.

Uses

- Thorium in cancer treatment and gas mantles
- Uranium in glass industry, medicines, nuclear fuel
- Plutonium in atomic reactors and bombs

Differences Between Lanthanoids and Actinoids

Lanthanoids fill 4f orbitals, actinoids fill 5f. Lanthanoids mostly +3 oxidation state, actinoids have wider range. Lanthanoids mostly non-radioactive, actinoids radioactive. Actinoids form more complexes and are more reactive.

Solved Examples

Example 1

Explain why actinoid contraction is greater than lanthanoid contraction and why transition metals form coloured compounds.

Solution:

Actinoid contraction is greater because 5f orbitals shield less effectively than 4f orbitals, causing a greater decrease in size. Transition metals form coloured compounds due to d–d electronic transitions where visible light is absorbed, and the complementary colour is observed.

Example 2

Complete the redox reaction: $2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow ?$

Solution:

$2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$

Practice Set

- **Level 1 (Easy):** Define lanthanoids and state their general electronic configuration.
- **Level 2 (Moderate):** Describe the lanthanoid contraction and its consequences.
- **Level 3 (Challenging):** Write the balanced chemical equation for the preparation of potassium permanganate from pyrolusite ore.

Answer Key

- **Level 1:** Lanthanoids are f-block elements filling 4f orbitals, with general electronic configuration [Xe] $4f^{1-14}$ $5d^{0-1}$ $6s^2$.
- **Level 2:** Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series due to poor shielding by 4f electrons. Consequences include similar properties among lanthanoids, difficulty in separation, and similar sizes of Zr and Hf.
- **Level 3:** $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$ (followed by electrolytic oxidation of K_2MnO_4 to $KMnO_4$)

Quick Reference Table

d-Block Elements

- General electronic configuration: (n-1)d^{1-10} ns^{1-2}
- Variable oxidation states due to ns and (n-1)d electrons
- High melting points and densities
- Form coloured compounds due to d–d transitions
- Examples: Fe, Cu, Zn

f-Block Elements

- General electronic configuration: (n-2)f^{1-14} (n-1)d^{0-1} ns^2
- Lanthanoids: 4f series, mainly +3 oxidation state

- Actinoids: 5f series, multiple oxidation states, radioactive
- Lanthanoid and actinoid contraction affect atomic sizes
- Examples: Ce, U, Pu

Common Mistakes and Misconceptions

- Incorrect electronic configurations for d- and f-block elements
- Confusing ionisation energies and oxidation states among transition elements
- Unbalanced chemical reactions of $KMnO_4$ and $K_2Cr_2O_7$
- Misunderstanding lanthanoid and actinoid contraction effects
- Assuming all lanthanoids are non-reactive or all actinoids are stable

Glossary

- **Transition Elements:** d-block elements with incomplete d-orbitals
- **Penultimate Shell:** The shell just inside the valence shell
- **Lanthanoid Contraction:** Decrease in size across lanthanoids due to poor shielding
- **Actinoid Contraction:** Similar decrease in size across actinoids
- **Variable Oxidation State:** Ability to exhibit multiple oxidation numbers
- **Interstitial Compounds:** Compounds formed when small atoms occupy spaces in metal lattices
- **Paramagnetism:** Magnetic property due to unpaired electrons
- **Diamagnetism:** Magnetic property due to paired electrons
- **Complex Ions:** Ions formed by coordinate bonding with ligands
- **Azo Compounds:** Organic compounds with –N=N– group