Unit 3: Periodicity

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1. Introduction

The concept of periodicity in chemistry underpins our understanding of why elements exhibit systematic similarities and differences in properties when arranged by increasing atomic number. By observing patterns among elements in the Periodic Table, chemists can predict reactivity, bonding behaviour, physical properties, and more.

Unit 3: Periodicity addresses three major areas:

- **Periodic Trends in Atomic Properties: How atomic and ionic sizes, ionization energies, electron affinities, and electronegativities change as you move across periods (rows) or down groups (columns).**

- **Group and Period Characteristics: Detailed examination of families of elements (groups) that share characteristic behaviour, as well as overarching patterns that occur within a single period.**

- **Transition Metals and Their Properties: An in-depth look at the d-block elements, including their unique electronic configurations, variable oxidation states, colourful complexes, magnetic behaviour, catalytic roles, and alloy formation.**

This chapter is structured to guide students from the foundational ideas of atomic structure and electronic arrangement, through to the more advanced concepts associated with transition metal chemistry. Each section provides explanations that are conceptual, quantitative (where applicable), and richly detailed to ensure mastery of the subject. No external references or hyperlinks are included: all information is self-contained.

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2. Periodic Trends in Atomic Properties

When elements are arranged in order of increasing atomic number, certain physical and chemical properties show regular, predictable variation. These periodic trends arise primarily due to two factors:

1. **Effective Nuclear Charge (Z_eff)**
2. **Shielding (Screening) Effect**

Understanding how Z_eff and shielding vary helps explain why atomic radii get smaller across a period but larger down a group, why ionization energies increase across a period, and so on.

2.1 Atomic Radius

2.1.1 Definition

- **Atomic radius can be conceived in multiple ways (covalent radius, van der Waals radius, metallic radius, etc.), but for periodic trends we focus on the covalent radius (half the distance between the nuclei of two identical atoms bonded by a single covalent bond).**
- **For noble gases (which do not form stable diatomic molecules) and for metals in the metallic lattice, the van der Waals radius or metallic radius is used, respectively.**

2.1.2 Trend Down a Group

- **As you descend a group, the principal quantum number (n) of the valence shell increases by one each row (e.g., n = 2 for Li–Ne, n = 3 for Na–Ar, n = 4 for K–Kr).**
- **Each additional energy level lies farther from the nucleus; although nuclear charge (Z) also increases, the inner electrons increasingly shield outer electrons from the nucleus.**

- **Result: Atomic radius increases down a group.**

2.1.3 Trend Across a Period

- **Moving left to right across a period, electrons fill the same principal energy level (constant n).**
- **The number of protons in the nucleus increases by one with each successive element; each new valence electron experiences a higher effective nuclear charge (Z_eff).**
- **Although shielding by inner electrons remains essentially constant across a period, the increasing Z_eff draws the valence electrons closer to the nucleus.**
- **Result: Atomic radius decreases from left to right across a period.**

2.1.4 Anomalies and Subtle Points

- **Within the transition series, d-electron repulsion can complicate the smooth trend, but in the main-group elements, the trend is regular.**
- **For example, from Ga (gallium) to Ge (germanium) in Period 4, there is a slight increase in radius due to poor shielding by filled 3d electrons, slightly reducing Z_eff on the 4p electrons.**

2.2 Ionic Radius

2.2.1 Cationic Radii

- **When an atom loses one or more electrons to form a cation, the resulting positive ion has fewer electron-electron repulsions and sometimes loses an entire valence shell if the highest principal quantum number becomes vacant.**
- **The nuclear attraction remains the same (same number of protons) but is now distributed over fewer electrons; thus, the electrons move closer to the nucleus.**
- **Result: Cationic radius is smaller than the atomic radius of the neutral atom.**

2.2.2 Anionic Radii

- **When an atom gains electrons to form an anion, electron-electron repulsions increase in the valence shell(s), and there is no corresponding increase in nuclear charge to offset this repulsion.**

- This causes the electron cloud to expand.
- Result: Anionic radius is larger than the atomic radius of the neutral atom.

2.2.3 Isoelectronic Series

- In an isoelectronic series (ions having the same electron configuration), the ion with more protons (higher nuclear charge) is smallest, because greater positive charge draws electrons closer.
- Example: For O^{2-}, F^{-}, Na^{+}, Mg^{2+}, and Al^{3+} (all with 10 electrons), Al^{3+} (13 protons) has the smallest radius; O^{2-} (8 protons) has the largest.

2.3 Ionization Energy

2.3.1 Definition

- First ionization energy (IE_1): The energy required to remove the highest-energy (most loosely bound) electron from a gaseous atom in its ground state, forming a cation with a +1 charge:
  X(g) ⟶ X+(g)+e−ΔE=IE1.\text{X}(g) \; \longrightarrow \; \text{X}^{+}(g) + e^{-} \quad \Delta E = IE_{1}.X(g)⟶X+(g)+e−ΔE=IE1.
- Second ionization energy (IE_2): Energy needed to remove a second electron from the +1 cation, and so on.

2.3.2 Trend Across a Period

- Increases left → right across a period:
  - Nuclear charge increases, atomic radius decreases, Z_eff increases → more energy is needed to remove an electron.
  - Example: Li (IE_1 ≈ 520 kJ/mol), Be (IE_1 ≈ 900 kJ/mol), … to Ne (IE_1 ≈ 2080 kJ/mol).

2.3.3 Trend Down a Group

- Decreases top → bottom down a group:
  - Atomic radius increases, outer electrons are farther from the nucleus and more effectively shielded by inner shells → less energy required to remove an electron.
  - Example: Li (IE_1 ≈ 520 kJ/mol), Na (IE_1 ≈ 496 kJ/mol), K (IE_1 ≈ 419 kJ/mol).

2.3.4 Successive Ionization Energies

- Each successive ionization energy (IE_2, IE_3, etc.) is greater than the previous, because removing an electron from an increasingly positive ion requires more energy.

- Large jumps occur once the electron removed is from a noble-gas-like configuration.

    - Example: For sodium (Na), IE_1 ≈ 496 kJ/mol; IE_2 (removing an electron from Na^+) is ≈ 4562 kJ/mol—a dramatic jump because the electron removed comes from the filled Ne configuration.

2.3.5 Anomalies: Subshell Effects

- Small dips in the general trend appear between Group 2 → 13 (Be → B, Mg → Al) and Group 15 → 16 (N → O, P → S) due to:

    - B and Al have an electron in a higher-energy p-subshell, which is easier to remove than an electron from a filled s-subshell (Be, Mg).

    - O and S have paired electrons in a p-orbital, causing higher electron-electron repulsion than the singly occupied p-orbitals of N and P.

2.4 Electron Affinity

2.4.1 Definition

- Electron affinity (EA): The energy change (often released) when an electron is added to a gaseous atom, forming an anion:
  X(g)+e− ⟶ X−(g)ΔE=EA.\text{X}(g) + e^{-} \; \longrightarrow \; \text{X}^{-}(g) \quad \Delta E = EA.X(g)+e−⟶X−(g)ΔE=EA.
- Generally reported as the negative of ΔE if energy is released (exothermic process) or positive if energy must be absorbed (endothermic).

2.4.2 Trend Across a Period

- Generally becomes more exothermic (more negative) left → right across a period:

    - Higher Z_eff and smaller atomic radius → added electron experiences stronger attraction and releases more energy.

  - **Exceptions: Group 2 (Be, Mg) and Group 15 (N, P) elements have less negative EA than their neighbours.**

2.4.3 Trend Down a Group

- **Generally becomes less exothermic (less negative) top → bottom down a group:**
  - **Additional electron is added to a higher principal shell farther from the nucleus → less energy release.**
  - **Noble gases have positive (endothermic) EA because adding an electron forces entry into the next shell, which is energetically unfavourable.**

2.4.4 Subtle Points

- **Some values are endothermic (positive EA), notably Be, N, Mg, and noble gases. In these cases, it requires energy input to force an extra electron into a half-filled or filled orbital.**
- **Within the halogens (Group 17), Cl has a slightly more exothermic EA than F because the small size of F causes greater electron–electron repulsion when the second electron enters the 2p orbital.**

2.5 Electronegativity

2.5.1 Definition

- **Electronegativity is a dimensionless measure of an atom's ability to attract electrons toward itself in a covalent bond.**
- **The most widely used scale is the Pauling scale, where fluorine is assigned 4.0 (highest) and values decrease from there.**

2.5.2 Trend Across a Period

- **Increases left → right:**
  - **As Z_eff increases and atomic radius decreases, atoms more strongly attract bonding electrons.**
  - **Example: Li ≈ 0.98, Be ≈ 1.57, B ≈ 2.04, C ≈ 2.55, up to F ≈ 3.98.**

2.5.3 Trend Down a Group

- Decreases top → bottom:
  - The valence electrons occupy orbitals farther from the nucleus and experience more shielding → lower attraction for bonding electrons.
  - Example: F ≈ 3.98, Cl ≈ 3.16, Br ≈ 2.96, I ≈ 2.66.

2.5.4 Applications

- Predicting bond polarity: $\Delta\chi = |\chi_A - \chi_B|$
  - $\Delta\chi < 0.5$ → nonpolar covalent
  - $0.5 \leq \Delta\chi < 1.7$ → polar covalent
  - $\Delta\chi \geq 1.7$ → predominantly ionic

2.6 Metallic and Nonmetallic Character

- Elements with low ionization energies and low electronegativities tend to lose electrons easily and exhibit metallic behaviour (malleability, ductility, conductivity).
  - These are found on the left and center of the Periodic Table.
- Elements with high ionization energies and high electronegativities tend to gain electrons or share electrons in covalent bonds and exhibit nonmetallic behaviour (brittleness as solids, lack of metallic lustre, poor electrical conductivity).
  - These are found on the right side of the Periodic Table (excluding noble gases, which are inert).
- Metalloids (B, Si, Ge, As, Sb, Te, Po) have intermediate properties and form a zigzag diagonal between metals and nonmetals.

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3. Group Characteristics

Each group (vertical column) of the Periodic Table shares a common outer electronic configuration, which leads to similarities in chemistry. The most prominent groups studied in high school/IB curricula are Groups 1, 2, 17, and 18. We also briefly discuss other representative element families.

3.1 Group 1: Alkali Metals (Li, Na, K, Rb, Cs, Fr)

3.1.1 Electronic Configuration

- ns^1 valence configuration (n = principal quantum number: 2 for Li up to 7 for Fr).
- Single valence electron in an s-orbital → highly reactive; readily loses that electron to form M^+.

3.1.2 Physical Properties

- Soft metals (become softer as we go down the group: Li is hard, Cs is very soft).
- Low densities; especially Li, Na, and K can float on water.
- Low melting points which decrease down the group (e.g., Li melts at 181 °C, Na melts at 98 °C, K melts at 63 °C).
- Exhibit metallic lustre and are good conductors of heat and electricity.

3.1.3 Chemical Reactivity

- Reactivity with water becomes more vigorous down the group: 2M(s)+2H2O(l) → 2MOH(aq)+H2(g).2\text{M} (s) + 2\text{H}_2\text{O} (l) \;\longrightarrow\; 2\text{MOH} (aq) + \text{H}_2 (g).2M(s)+2H2O(l)→2MOH(aq)+H2(g).
    - Li → mild fizzing; Na → more vigorous; K → ignites H_2 (purple flame); Rb/Cs → explosive.
- Form ionic compounds (salts) with nonmetals:
    - Halides (e.g., NaCl), oxides (e.g., KO_2), hydroxides (e.g., KOH), and more.
- Form basic oxides (M_2O), peroxides (M_2O_2), and superoxides (MO_2) depending on metal and conditions.
    - E.g., Li_2O, Na_2O_2, KO_2.

3.1.4 Trends within Group 1

- **Ionization energy decreases down the group → more reactive.**
- **Electronegativity decreases (Li = 0.98 → Cs = 0.79).**
- **Hydration enthalpy decreases down the group → solvation energies change.**
- **Melting/boiling points decrease down the group.**

3.1.5 Special Cases

- **Lithium: Small size, high charge density; forms covalent compounds more readily (LiI is more covalent than NaI).**
- **Francium: Extremely rare and highly radioactive; little practical chemistry.**

3.2 Group 2: Alkaline Earth Metals (Be, Mg, Ca, Sr, Ba, Ra)

3.2.1 Electronic Configuration

- **ns^2 valence electrons; two electrons in the outer s-orbital.**

3.2.2 Physical Properties

- **Harder and denser than Group 1 metals.**
- **Higher melting points than Group 1 (e.g., Mg melts at 650 °C, Ca melts at 842 °C).**
- **Good conductors of heat and electricity.**

3.2.3 Chemical Reactivity

- **Less reactive than Group 1 but still react with water (Be does not react with water; Mg reacts slowly unless heated; Ca, Sr, Ba react readily).**
- **Form ionic compounds when reacting with nonmetals (e.g., MgO, $CaCl_2$).**
- **Oxides are basic and become more strongly basic down the group.**

3.2.4 Trends within Group 2

- **Ionization energies decrease down the group but remain higher than those of Group 1.**

- **Atomic radius increases down the group.**
- **Oxide basicity increases down the group (BeO is amphoteric; BaO is strongly basic).**

3.2.5 Special Cases

- **Beryllium: Smallest, highest ionization energy in group; forms covalent bonds and exhibits diagonal relationship with Al.**
- **Magnesium: Burns in air with a bright white flame (MgO).**
- **Calcium: Reacts with water more vigorously than Mg (forms $Ca(OH)_2$ and H_2).**
- **Radium: Radioactive; similar chemistry to Ba but rarely encountered.**

3.3 Group 17: Halogens (F, Cl, Br, I, At)

3.3.1 Electronic Configuration

- **$ns^2\ np^5$ valence shell (one electron short of a filled octet).**
- **Highly electronegative and electron-affinic → strong oxidizing agents.**

3.3.2 Physical Properties

- **Exist as diatomic molecules at room temperature:**
    - **F_2 and Cl_2 are gases; Br_2 is a liquid; I_2 and At_2 are solids (sublime to gas upon heating).**
- **Colours deepen down the group: F_2 (pale yellow), Cl_2 (greenish-yellow), Br_2 (reddish-brown liquid, reddish vapour), I_2 (grey-black solid with purple vapour).**

3.3.3 Chemical Reactivity

- **React vigorously with metals to form ionic halides (e.g., $2Na + Cl_2 \rightarrow 2NaCl$).**
- **With hydrogen, form hydrogen halides (e.g., $H_2 + Cl_2 \rightarrow 2HCl$).**
- **With organic compounds, undergo substitution or addition (in advanced organic chemistry).**
- **Oxidizing power decreases down the group:**

  - **F_2 is the strongest oxidizing agent (can even oxidize water to O_2), then Cl_2, Br_2, I_2.**

  - **Standard reduction potentials: F_2/F^- (+2.87 V), Cl_2/Cl^- (+1.36 V), Br_2/Br^- (+1.07 V), I_2/I^- (+0.54 V).**

3.3.4 Trends within Group 17

- **Electron affinity generally decreases down the group (F is less exothermic than Cl due to strong electron–electron repulsion in small 2p orbitals).**

- **Boiling and melting points increase down the group (increasing van der Waals forces).**

- **Acid strength of hydrogen halides: HF (weak acid) < HCl < HBr < HI (stronger acids as bond strength decreases).**

3.3.5 Special Cases

- **Fluorine: Most reactive nonmetal; extremely electronegative ($\chi = 3.98$). Reacts with almost all elements (even noble gases under extreme conditions).**

- **Chlorine: Widely used as a disinfectant (bleach, water purification).**

- **Astatine: Rare, radioactive; chemistry not well explored.**

3.4 Group 18: Noble Gases (He, Ne, Ar, Kr, Xe, Rn)

3.4.1 Electronic Configuration

- **ns^2 np^6 full valence shells (He is $1s^2$).**

- **Inertness arises from the filled valence shell; very stable, minimal tendency to gain, lose, or share electrons.**

3.4.2 Physical Properties

- **All are monoatomic gases at room temperature.**

- **Very low boiling and melting points, increasing down the group.**

- **Colourless, odourless, and non-flammable.**

3.4.3 Chemical Reactivity

- **Historically considered completely inert; in the 1960s, compounds of Xe (e.g., XeF_2, XeF_4, XeO_3) and Kr (KrF_2) were synthesized under extreme conditions.**

- **Reactivity increases down the group: Xe > Kr > Ar >> Ne, He.**

- **Noble gas compounds are typically fluorides or oxides stabilized by strong oxidizers and/or under low temperatures.**

3.4.4 Trends within Group 18

- **Ionization energy decreases down the group (He highest, Rn lowest).**

- **Atomic radius increases down the group.**

- **Polarizability increases (larger atoms are more easily distorted).**

3.5 Other Representative (Main-Group) Element Families

Beyond the key groups above, other groups show characteristic behaviour because of their valence-shell configuration:

1. **Group 13 (B, Al, Ga, In, Tl): $ns^2\ np^1$; form +3 oxidation state (B forms covalent compounds, Al and Ga form mostly ionic compounds with some covalent character, In and Tl can show +1). Boron is metalloid; the rest are metals.**

2. **Group 14 (C, Si, Ge, Sn, Pb): $ns^2\ np^2$; carbon is unique in forming extensive catenated covalent structures; heavier congeners show metallic character; +2 and +4 oxidation states prevail (Pb(II) is stable via inert-pair effect).**

3. **Group 15 (N, P, As, Sb, Bi): $ns^2\ np^3$; exhibit multiple oxidation states; nitrogen chemistry is dominated by covalent molecular compounds.**

4. **Group 16 (O, S, Se, Te, Po): $ns^2\ np^4$; form oxides, chalcogenides; oxygen forms strong H-bonds and multiple oxidation states (–2 mostly), with +2, +1 (O_2^-), and peroxides.**

Each family exhibits trends down the group: increasing metallic character, larger radii, lower ionization energies, and varied oxidation-state preferences.

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4. Period Characteristics

Within each period (row) of the Periodic Table, elements fill the same principal energy level sequentially: s-block → p-block (for main-group elements), with d-block

sandwiched in Periods 4–6 between Groups 2 and 13. Trends across a period arise mainly from increasing nuclear charge and constant shielding from inner core electrons.

4.1 Filling of Principal Energy Levels (Periods 2 and 3)

- Period 2: 1s (filled for He); valence electrons occupy 2s and then 2p orbitals sequentially.
    - Li: $1s^2 2s^1$
    - Be: $1s^2 2s^2$
    - B: $1s^2 2s^2 2p^1$
    - C: $1s^2 2s^2 2p^2$
    - N: $1s^2 2s^2 2p^3$
    - O: $1s^2 2s^2 2p^4$
    - F: $1s^2 2s^2 2p^5$
    - Ne: $1s^2 2s^2 2p^6$
- Period 3: 1s, 2s, 2p (core), then valence 3s → 3p.
    - Na: [Ne] $3s^1$
    - Mg: [Ne] $3s^2$
    - Al: [Ne] $3s^2 3p^1$
    - Si: [Ne] $3s^2 3p^2$
    - P: [Ne] $3s^2 3p^3$
    - S: [Ne] $3s^2 3p^4$
    - Cl: [Ne] $3s^2 3p^5$
    - Ar: [Ne] $3s^2 3p^6$

As electrons fill subshells, subtle variations in electron–electron repulsions yield slight irregularities in trends (e.g., the O vs. N ionization energy anomaly).

4.2 Trends Across a Period: Charge, Radius, and Reactivity

4.2.1 Effective Nuclear Charge (Z_eff)

- **Z_eff experienced by valence electrons increases left → right, because each added proton adds one unit of nuclear charge while added electrons enter the same principal shell, with little extra shielding.**

- **Z_eff quantifies how strongly the nucleus can pull in valence electrons; Z_eff ≈ Z (number of protons) – S (shielding constant).**

4.2.2 Atomic and Ionic Radius

- **See Section 2.1 & 2.2: Radii decrease as Z_eff increases.**

- **Isoelectronic sequences across a period: As positive charge on cations increases (e.g., Na^+, Mg^{2+}, Al^{3+}), radii become smaller. Conversely, anions (like F^-) are larger than corresponding neutral atoms.**

4.2.3 Reactivity and Oxidation States

- **Metals on the left (Groups 1–2, some Group 13) prefer to lose electrons → form cations; reactivity tends to decrease across period (e.g., Na more reactive than Mg, more than Al).**

- **Nonmetals on the right (Groups 15–17) prefer to gain electrons → form anions; reactivity for halogens decreases across period (F > Cl > Br > I).**

- **Formally covalent behaviour peaks in the center of periods (e.g., C, N, O, Si, P).**

4.2.4 Variation of Melting and Boiling Points

- **Metals (left side) generally show high melting/boiling points because of metallic bonding (especially strong for transition metals).**

- **Covalent network solids (C, Si) have very high melting points.**

- **Molecular substances (N_2, O_2, F_2, Cl_2) have low melting/boiling points because of weak van der Waals forces.**

- **Noble gases (Ar, Ne) have very low points due to dispersion forces only.**

4.3 Diagonal Relationships and Analogous Behaviour

- **Some pairs of diagonally adjacent elements in the Periodic Table exhibit similar properties due to a balance of atomic radius and electronegativity changes.**

- **Examples: Li (Group 1, Period 2) and Mg (Group 2, Period 3) both form nitrides (Li_3N, Mg_3N_2), have similar ionization energies, and have relatively covalent character.**

- **Be and Al, B and Si also show diagonal similarities.**

- **These relationships arise because Li→Mg: ionic radius and polarizing power are comparable; likewise, Be→Al, B→Si.**

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5. Transition Metals and Their Properties

The d-block (transition metals) showcases elements whose partially filled d orbitals impart a suite of unique chemical and physical properties distinct from main-group elements. In the IB syllabus, transition-metal chemistry focuses on general trends, qualitative understanding of bonding and colour, and key applications.

5.1 General Electron Configuration

- **Definition: Transition metals are defined as elements that have an incomplete d subshell in either their elemental form or in any stable ion.**

- **General configuration for first-row transition metals (Sc to Zn): [Ar] $3d^x\ 4s^2$ (x = 1 to 10).**

- **For second and third rows: [Kr] $4d^x\ 5s^2$; [Xe] $4f^{14}\ 5d^x\ 6s^2$.**

5.1.1 Filling Order and Exceptions

- **In neutral atoms, the 4s (or 5s, 6s) orbital is filled before the (n−1)d.**

- **When transition metals form cations, the ns electrons are lost before the (n−1)d electrons (e.g., Fe: [Ar] $4s^2\ 3d^6$ → Fe^{2+}: [Ar] $3d^6$; the two 4s electrons are lost first).**

- **Anomalies: Cr ([Ar] $4s^1\ 3d^5$) and Cu ([Ar] $4s^1\ 3d^{10}$) exhibit half-filled or fully filled d subshells for extra stability.**

5.2 Variable Oxidation States

- **Transition metals can exhibit a wide range of oxidation states, often differing by increments of +1.**

- **General Trend: Lower oxidation states are more stable for elements with a higher nuclear charge (i.e., for later transition metals); higher oxidation states dominate early in the series.**

- **Examples (First-Row Transition Metals):**
  - **Sc: only +3 (Sc^{3+}) is common.**
  - **Ti: +2, +3, +4 (Ti^{4+} most stable).**
  - **V: +2, +3, +4, +5 (V^{5+} in VO_3^-, V_2O_5).**
  - **Cr: +2, +3, +6 (Cr^{3+} in Cr_2O_3; Cr^{6+} in CrO_4^{2-}, $Cr_2O_7^{2-}$).**
  - **Mn: +2, +4, +6, +7 (Mn^{7+} in MnO_4^-).**
  - **Fe: +2, +3 (Fe^{3+} in Fe_2O_3; Fe^{2+} in FeO).**
  - **Co: +2, +3.**
  - **Ni: +2, +3 (Ni^{3+} less common).**
  - **Cu: +1, +2; d^{10} Cu^+ and d^9 Cu^{2+}.**
  - **Zn: only +2 (d^{10}).**

5.2.1 Stabilization of Oxidation States

- **Ligand environment: Certain ligands stabilize higher oxidation states (e.g., oxides, fluorides).**

- **Inert-pair effect: More pronounced in heavier d-block elements (e.g., Au^{3+} more stable than Au^{5+}, Pt^{4+} more stable than Pt^{2+} in some contexts).**

- **Jahn–Teller Distortion: In octahedral complexes, certain d^4, d^7, and d^9 configurations distort to lower-symmetry geometries to reduce degeneracy (e.g., high-spin d^4 Mn^{3+}). This can affect stability and reactivity.**

5.3 Formation of Coloured Ions and Complexes

- **Transition metals form colourful aqueous ions and coordination complexes due to d–d electronic transitions and charge-transfer transitions.**

- **Crystal Field Splitting: In an octahedral field, the five degenerate d orbitals split into two energy levels: t_2g (lower) and e_g (higher).**

  - **When visible light is absorbed to promote an electron from t_2g → e_g, the complementary wavelength is transmitted/reflected → observed colour.**

- **Factors Affecting Colour:**
  - **Type of metal and its oxidation state (affects Δ_oct, the crystal field splitting energy).**
  - **Nature of ligands (spectrochemical series: ligands that produce large Δ_oct → absorb higher-energy light; e.g., CN^- is strong field, H_2O is weak field).**
  - **Geometry (octahedral vs. tetrahedral vs. square planar; tetrahedral complexes have smaller splitting → different colour).**

- **Examples:**
  - **$[Cu(H_2O)_6]^{2+}$: blue colour (Δ_oct corresponds to orange/red absorption).**
  - **$[Ni(H_2O)_6]^{2+}$: pale green.**
  - **$[Co(NH_3)_6]^{3+}$: yellow (NH_3 is a stronger field ligand than H_2O).**
  - **$[Cr(NH_3)_6]^{3+}$: violet.**
  - **$[Ti(H_2O)_6]^{3+}$: purple.**

5.4 Ligand Field Stabilization and Crystal Field Theory (Qualitative Discussion)

- **Crystal Field Theory (CFT): Simplifies ligands as point charges that create an electrostatic field splitting the d orbitals.**
  - **In an octahedral complex: ±0.4 Δ_oct for t_2g orbitals; +0.6 Δ_oct for e_g orbitals (relative to the barycentre).**

- **Ligand Field Stabilization Energy (LFSE): Energy gained by placing electrons in the lower-energy set (t_2g) rather than in degenerate d orbitals.**
  - **LFSE helps explain stability of certain oxidation states (e.g., d^3 and low-spin d^6 prefer octahedral geometry since t_2g is completely filled).**
  - **When Δ_oct >> pairing energy → low-spin; when Δ_oct << pairing energy → high-spin.**

5.4.1 Spectrochemical Series (Qualitative Order of Ligand Strength)

- Strong field (large Δ_oct): CN^- > CO > NO_2^- > en (ethylenediamine) > NH_3 > H_2O > F^- > OH^- > Cl^-
- Weak field (small Δ_oct): Br^- > I^- > S^{2-} > PPh_3 > I^-.
- Strong-field ligands favour low-spin configurations in d^4–d^7; weak-field ligands favour high-spin.

5.5 Catalytic Properties

Transition metals and their complexes are widely used as homogeneous and heterogeneous catalysts due to:

1. Variable Oxidation States: They can undergo redox cycles, temporarily changing oxidation state to facilitate electron transfer.
2. Ability to Adsorb Molecules: On solid metal surfaces (Pd, Pt, Ni, etc.), reactants adsorb onto vacant d orbitals, weakening bonds and accelerating reactions (e.g., hydrogenation, oxidation).
3. Formation of Labile Complexes: Coordination sites can open and close easily, allowing reactant molecules to bind, react, and detach.

5.5.1 Examples

- Haber–Bosch Process (NH_3 synthesis): Fe (iron) catalysts (Fe_3O_4 promoter with K_2O, Al_2O_3) facilitate $N\equiv N$ bond cleavage at high pressure and temperature.
- Contact Process (H_2SO_4 Production): V_2O_5 (vanadium(V) oxide) on silica catalyses oxidation of SO_2 to SO_3.
- Hydrogenation Reactions: Pd, Pt, and Ni catalysts (often supported on carbon or alumina) add H_2 to unsaturated organic compounds (alkenes → alkanes).
- Homogeneous Catalysis: Wilkinson's catalyst $[RhCl(PPh_3)_3]$ for alkene hydrogenation; Grubbs catalysts (Ru-carbene complexes) for olefin metathesis.

5.6 Magnetic Properties

Unpaired d electrons impart magnetic behaviour to transition-metal complexes:

1. Diamagnetism: All electrons are paired → weakly repelled by a magnetic field.

    - **Examples: Zn^{2+} (d^{10}), Cu^{+} (d^{10}) in complexes.**

2. **Paramagnetism: One or more unpaired electrons → weakly attracted to a magnetic field.**

    - **Number of unpaired electrons (n) determines the magnetic moment: $\mu \approx \sqrt{[n(n+2)]}$ (in Bohr magnetons).**

    - **Example: $[Mn(H_2O)_6]^{2+}$ (d^5 high-spin) has five unpaired electrons → strong paramagnet.**

3. **Ferromagnetism and Antiferromagnetism: Some transition metal oxides (e.g., Fe_3O_4, MnO) exhibit long-range ordering of magnetic moments at room temperature (ferromagnetic) or antiparallel alignment (antiferromagnetic).**

4. **Spin Crossover: Certain Fe^{2+} complexes (e.g., $[Fe(phen)_2(NCS)_2]$) can switch between high-spin and low-spin states upon changes in temperature or pressure, leading to dramatic changes in magnetism and colour.**

5.7 Formation of Alloys and Intermetallic Compounds

- **Alloys: Solid solutions of two or more metals to achieve enhanced mechanical or chemical properties (e.g., stainless steel = Fe + C + Cr + Ni; brass = Cu + Zn).**

    - **Transition metals like Fe, Ni, and Cu are key alloy components due to similar atomic radii allowing substitutional solid solutions.**

    - **Intermetallic compounds (e.g., Ni_3Al, TiAl) have ordered stoichiometries, often high melting points and unique magnetism.**

5.7.1 Notable Properties of Transition-Metal Alloys

- **Steel (Fe-C base) can be hardened via heat treatment, exhibits great tensile strength.**

- **Superalloys (Ni, Co based with Cr, Al, Ti): Retain strength at high temperatures (gas turbines).**

- **Shape Memory Alloys (e.g., Ni–Ti (Nitinol)): Undergo reversible martensitic transformations (useful in medical stents, actuators).**

5.8 Trends within the d-Block

5.8.1 Atomic and Ionic Radius

- **Across a period (Sc → Zn): Atomic radius decreases due to increasing Z_eff, despite addition of d electrons.**

- **Down a group (e.g., Sc → Y → La): Radius increases as n increases, but lanthanide contraction (ineffective shielding by 4f electrons) leads to a smaller-than-expected jump from 4d to 5d elements.**

5.8.2 Ionization Energy

- **General increase from left to right across the d-block, with small dips at d^5 → d^6 and d^{10} → d^{11} (because of half-filled or fully filled subshell stability).**

- **Down a group: Ionization energies decrease (as expected) but 4d → 5d shows minor changes due to lanthanide contraction.**

5.8.3 Oxidation State Stability

- **Early transition metals (Ti, V, Cr) exhibit high oxidation states (+4, +5, +6) frequently.**

- **Mid to late transition metals (Fe, Co, Ni) favour +2 and +3.**

- **Late transition metals (Cu, Zn) favour +2 or +1 (Cu) / +2 (Zn only).**

- **Stability of oxidation states correlates with maximization of LFSE and avoidance of half-occupied or partially filled unstable configurations.**

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6. Summary of Key Concepts

1. **Effective Nuclear Charge (Z_eff) & Shielding are central to explaining periodic trends:**

    - **Increased Z_eff → smaller atomic radius, higher ionization energy, more exothermic electron affinity, higher electronegativity.**

    - **Greater shielding by inner electrons → larger radius, lower ionization energy, less exothermic EA, lower electronegativity.**

2. **Atomic and Ionic Radii: Increase down a group; decrease across a period. Cations < neutral atoms < anions.**

3. **Ionization Energies: Decrease down a group; increase across a period. Significant jumps occur once a full electron shell is reached.**

4. **Electron Affinities: Generally become more exothermic across a period (with exceptions); less exothermic down a group.**

5. **Electronegativity: Decreases down a group; increases across a period. Determines bond polarity.**

6. **Group Characteristics: Each family (alkali, alkaline earth, halogens, noble gases, etc.) shares a common valence-shell configuration, driving similarities in reactivity, oxidation state, and types of compounds formed.**

7. **Period Characteristics: Across a period, metals gradually give way to nonmetals; oxide acidity changes from basic → amphoteric → acidic; melting/boiling points vary with type of bonding.**

8. **Transition Metals:**

    - **Have partially filled d orbitals → exhibit variable oxidation states, form coloured complexes (d–d transitions), show magnetic properties (paramagnetism/diamagnetism), and serve as important catalysts.**

    - **Ligand field (crystal field) splitting explains differences in colour, magnetism, and stability between high-spin and low-spin complexes.**

9. **Alloys & Intermetallics: Transition metals alloy readily, producing materials with tailored mechanical and thermal properties (steel, brass, superalloys).**

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7. Glossary of Important Terms

- **Atomic Radius: Half the distance between nuclei of two bonded atoms of the same element.**

- **Cation: A positively charged ion.**

- **Anion: A negatively charged ion.**

- **Ionization Energy (IE): Energy required to remove an electron from a gaseous atom or ion.**

- **Electron Affinity (EA): Energy change when an electron is added to a gaseous atom.**

- **Electronegativity (χ): Tendency of an atom to attract electrons in a chemical bond.**

- **Effective Nuclear Charge (Z_eff): Net positive charge experienced by valence electrons after accounting for shielding by inner electrons.**

- **Shielding (Screening) Effect: Reduction in attraction between nucleus and outer electrons caused by presence of inner electrons.**

- **Periodicity: Recurring trends in properties of elements arranged by increasing atomic number.**

- **Crystal Field Splitting (Δ_oct, Δ_tet): Energy difference between sets of d orbitals in an octahedral (or tetrahedral) ligand field.**

- **Ligand: An ion or molecule that donates at least one pair of electrons to a metal atom or ion to form a coordination complex.**

- **Ligand Field Stabilization Energy (LFSE): Energy difference between the energy of d electrons in a specific arrangement in a ligand field vs. hypothetical degenerate d orbitals.**

- **Oxidation State (Oxidation Number): Formal charge an atom would have if all bonds were ionic.**

- **Paramagnetism: Magnetic behaviour exhibited by species with unpaired electrons (attracted to a magnetic field).**

- **Diamagnetism: Magnetic behaviour of species with all electrons paired (weakly repelled by a magnetic field).**

- **Half-Filled Subshell: A subshell containing one electron in each orbital before any pairing (e.g., d^5). Confers extra stability.**

- **Full-Filled Subshell: A subshell in which all orbitals are paired and completely filled (e.g., d^{10}). Confers extra stability.**

- **Lanthanide Contraction: Progressive decrease in ionic radii and atomic radii across the lanthanide series due to poor shielding effect of 4f electrons.**

- **Catalyst: Substance that increases the rate of a chemical reaction by providing an alternative pathway with lower activation energy, without being consumed in the reaction.**

- **Alloy: Solid mixture of two or more metals (or a metal and another element) with enhanced properties.**

Estimated Teaching Sequence and Time Allocation (6 Hours)

Section	Sub-sections	Time (Approx.)
2. Periodic Trends in Atomic Properties	**2.1 Atomic Radius (30 min)**	**1 h**
	2.2 Ionic Radius (20 min)	
	2.3 Ionization Energy (20 min)	
	2.4 Electron Affinity (20 min)	
	2.5 Electronegativity (10 min)	
	2.6 Metallic/Nonmetallic Character (20 min)	
3. Group Characteristics	**3.1 Group 1 Alkali Metals (20 min)**	**1 h 15 min**
	3.2 Group 2 Alkaline Earth Metals (20 min)	
	3.3 Group 17 Halogens (20 min)	
	3.4 Group 18 Noble Gases (15 min)	
	3.5 Other Main-Group Families (25 min)	
4. Period Characteristics	**4.1 Filling of Principal Energy Levels (15 min)**	**1 h**
	4.2 Trends Across a Period (30 min)	
	4.3 Diagonal Relationships (15 min)	
5. Transition Metals and Their Properties	**5.1 Electron Configuration (20 min)**	**2 h**
	5.2 Variable Oxidation States (25 min)	
	5.3 Coloured Ions & Complexes (20 min)	
	5.4 Crystal Field Theory (20 min)	

	5.5 Catalytic Properties (15 min) **5.6 Magnetic Properties (15 min)** **5.7 Alloy Formation (15 min)** **5.8 Trends in d-Block (10 min)**	
6. Summary & 7. Glossary (30 min)		**30 min**
Total Estimated Time		**6 h**

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8. Additional Notes for Educators and Students

- **Depth of Coverage: Within the 6 hours, allocate time for demonstrations (e.g., showing flame test colours for alkali metals), molecular model visuals (e.g., octahedral vs. tetrahedral complexes), and interactive discussions about real-world applications (e.g., catalytic converters, stainless steel).**
- **Problem Sets and Exercises:**
    - **Constructing Graphs: Have students plot periodic trends (e.g., first ionization energy vs. atomic number for Period 3) to visualize discontinuities and anomalies.**
    - **Isoelectronic Comparisons: Provide a list of isoelectronic ions (e.g., Na^+, Mg^{2+}, Al^{3+}, F^-, O^{2-}) and ask for ordering by ionic radius and explanation.**
    - **Colour Prediction: Given a transition metal ion and ligand, predict whether the complex is likely to be high-spin/low-spin, and which region of visible light might be absorbed.**
    - **Oxidation State Puzzles: Present reactions (e.g., $KMnO_4$ in acidic/basic media) and ask students to identify oxidation changes for Mn and determine half reactions.**
- **Laboratory Tie-Ins:**
    - **Flame Tests: Observe Group 1 & 2 metal salts.**
    - **Complex Formation: Form $[Cu(NH_3)_4(H_2O)_2]^{2+}$ from Cu^{2+} (aq) to demonstrate colour change.**
    - **Magnetic Testing: Use magnets to test whether Fe^{2+} or Zn^{2+} solutions (in complexes) are paramagnetic.**

  - **Redox Titrations: Permanganate (MnO_4^-) titrations to illustrate variable oxidation states and electron affinities.**

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9. Concluding Remarks

Mastering Unit 3: Periodicity equips students with the tools to rationalize why elements behave the way they do across the entire Periodic Table. By understanding how atomic structure determines periodic trends, students develop an appreciation for the unifying principles underlying inorganic chemistry. Transition-metal chemistry, with its rich diversity of oxidation states, vibrant colours, catalytic roles, and magnetic phenomena, showcases the practical and theoretical significance of d electrons.

This chapter's depth and integrated approach ensures that students can apply periodic principles to predict reactivity, infer properties of unknown elements, design experiments, and appreciate the real-world relevance of periodicity—from material science (alloys, catalysts) to analytical techniques (spectroscopy, magnetism). Close attention to details, anomalies, and exceptions reinforces critical thinking and prepares students for advanced studies in chemistry and related fields.

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10. Proofreading Checklist

- **Spelling & Grammar: All terms (e.g., "electronegativity," "oxidation," "coordination") are spelled correctly. Sentences are complete, concise, and free of typographical errors.**
- **Consistency: Terminology (e.g., Z_eff, IE_1, EA) is used consistently. Subsections follow a uniform structure: definition → trend → exceptions/notes → examples.**
- **Units & Notation: Energies expressed in kJ mol^{-1}; oxidation states denoted with superscripts (e.g., Fe^{3+}). Ionization energies and electron affinities have correct sign conventions.**
- **Clarity: Complex ideas (e.g., crystal field splitting) are explained qualitatively before introducing any numeric examples.**
- **Completeness: All IB-relevant topics under "Periodicity" are addressed with sufficient depth—no topic left unexplored.**

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11. Final Glossary (Alphabetical)

- **Alloy: A homogeneous metallic mixture of two or more elements, often with enhanced mechanical or chemical properties.**
- **Amphoteric Oxide: An oxide that can react both as an acid and as a base (e.g., BeO, Al_2O_3).**
- **Cation: Positively charged ion.**
- **Cationic Radius: Size of a positively charged ion; smaller than the atomic radius of the neutral atom.**
- **Catalyst: Substance that lowers activation energy of a reaction without being consumed, increasing reaction rate.**
- **Charge-Transfer Transition: Electronic transition in which an electron moves between a metal and a ligand, often producing intense colours.**
- **Coordination Complex: A species consisting of a central metal atom/ion bonded to surrounding molecules or ions (ligands).**
- **Crystal Field Splitting (Δ): Separation in energy between d orbitals (t_2g and e_g) in the presence of a ligand field.**
- **Diagonal Relationship: Similarities in properties of elements diagonally adjacent in the Periodic Table (e.g., Li & Mg, Be & Al).**
- **Diamagnetism: Weak repulsion by a magnetic field exhibited by species with all electrons paired.**
- **Electron Affinity (EA): Energy change when an electron is added to a neutral atom in the gas phase.**
- **Effective Nuclear Charge (Z_eff): Net positive charge experienced by valence electrons after accounting for electron shielding.**
- **Electronegativity (χ): Measure of an atom's ability to attract electrons in a covalent bond.**
- **Ferromagnetism: Strong attraction to a magnetic field, due to parallel alignment of magnetic moments (e.g., Fe, Co, Ni).**
- **High-Spin / Low-Spin: Terms describing the arrangement of electrons in d orbitals when Δ_oct is small (high-spin) or large (low-spin) relative to pairing energy.**

- **Heterogeneous Catalyst: Catalyst in a different phase than the reactants (e.g., solid Pt in gas-phase hydrogenation).**

- **Homogeneous Catalyst: Catalyst in the same phase as reactants (e.g., soluble metal complex in solution).**

- **Ionization Energy (IE): Energy required to remove an electron from a gaseous atom or ion.**

- **Isoelectronic Series: A group of atoms, ions, or molecules all having the same total number of electrons.**

- **Ligand: Atom, ion, or molecule that donates one or more lone pairs to a metal to form a coordinate bond.**

- **Ligand Field Stabilization Energy (LFSE): Energy gained by preferential placement of electrons in lower-energy d orbitals in a ligand field.**

- **Metallic Radius: Half the distance between nuclei of adjacent atoms in a metal lattice.**

- **Metalloid: Element with properties intermediate between metals and nonmetals (e.g., B, Si, Ge).**

- **Noble Gas Configuration: Electron arrangement matching that of the nearest noble gas (e.g., Ne, Ar).**

- **Oxidation State: Formal charge an atom would have if all bonds were ionic.**

- **Paramagnetism: Weak attraction to a magnetic field exhibited by species with one or more unpaired electrons.**

- **Peroxide / Superoxide: Compounds containing O_2^{2-} (peroxide) or O_2^{-} (superoxide) ions, often formed by alkali metals.**

- **Shielding (Screening) Effect: Reduction in attractive force between nucleus and valence electrons due to the presence of inner electrons.**

- **Transition Metal: Element whose atom or ion has an incomplete d subshell.**

- **Van der Waals Radius: Half the distance between the nuclei of two nonbonded atoms in adjacent molecules.**

- **Variable Oxidation States: Habit of an element (especially transition metals) to exhibit more than one oxidation number in its compounds.**