

## 5 MARK QUESTIONS

### 1. Explain the classification of elements into s-, p-, d-, and f-blocks with examples.

The modern periodic table classifies elements into four blocks—s, p, d, and f—based on the subshell (orbital) being filled by the outermost electrons, which determines their chemical properties and position.

- **s-block:** Elements where the valence electrons occupy the s-subshell (which can hold up to 2 electrons). These are groups 1 (alkali metals) and 2 (alkaline earth metals), plus hydrogen and helium. They are highly reactive metals (except helium, a noble gas). Examples: Sodium (Na, [Ne] 3s<sup>1</sup>) in group 1, and Calcium (Ca, [Ar] 4s<sup>2</sup>) in group 2. s-block elements lose electrons easily to form cations.
- **p-block:** Elements filling the p-subshell (up to 6 electrons). These span groups 13 to 18, including metals, non-metals, and metalloids. They show diverse properties: metals like aluminum, non-metals like oxygen, and noble gases like neon. Examples: Carbon (C, [He] 2s<sup>2</sup> 2p<sup>2</sup>) in group 14, and Chlorine (Cl, [Ne] 3s<sup>2</sup> 3p<sup>5</sup>) in group 17. p-block elements can gain or share electrons, forming anions or covalent bonds.
- **d-block:** Transition metals where the d-subshell is being filled (up to 10 electrons). These are groups 3 to 12, characterized by variable oxidation states, colored compounds, and catalytic properties due to partially filled d-orbitals. Examples: Iron (Fe, [Ar] 4s<sup>2</sup> 3d<sup>6</sup>) in group 8, and Copper (Cu, [Ar] 4s<sup>1</sup> 3d<sup>10</sup>) in group 11. The d-electrons participate in bonding, leading to complex formation.
- **f-block:** Inner transition metals, including lanthanides (elements 58-71) and actinides (90-103), where the f-subshell is filled (up to 14 electrons). They are placed below the main table. These elements have similar properties due to f-orbital shielding, showing +3 oxidation states commonly. Examples: Cerium (Ce, [Xe] 6s<sup>2</sup> 4f<sup>1</sup> 5d<sup>1</sup>) in lanthanides, and Uranium (U, [Rn] 7s<sup>2</sup> 5f<sup>3</sup> 6d<sup>1</sup>) in actinides. f-block elements are often radioactive and used in nuclear applications.

This classification reflects the Aufbau principle, where electrons fill orbitals in order of increasing energy, influencing reactivity and periodicity.

### 2. Discuss the rules governing electronic configuration of elements.

Electronic configuration describes the distribution of electrons in atomic orbitals, governed by quantum mechanical principles to achieve the lowest energy state. The key rules are:

1. **Aufbau Principle (Building-Up Principle):** Electrons fill orbitals starting from the lowest energy level. The order is 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p. This is based on the (n + l) rule, where n is the principal quantum number and l is the azimuthal quantum number; lower (n + l) fills first, and for ties, lower n fills first.
2. **Pauli Exclusion Principle:** No two electrons in an atom can have the same set of four quantum numbers (n, l, m<sub>l</sub>, m<sub>s</sub>). Thus, each orbital holds a maximum of two electrons with opposite spins (m<sub>s</sub> = +1/2 or -1/2).

- 3. Hund's Rule of Maximum Multiplicity:** Electrons fill degenerate orbitals (same energy, e.g., three p-orbitals) singly first, with parallel spins, before pairing up. This minimizes electron-electron repulsion and maximizes spin multiplicity for stability.

Exceptions occur due to extra stability of half-filled or fully filled subshells. For example, Chromium (Cr) is [Ar] 4s<sup>1</sup> 3d<sup>5</sup> instead of [Ar] 4s<sup>2</sup> 3d<sup>4</sup>, as half-filled d-subshell is stable. Similarly, Copper (Cu) is [Ar] 4s<sup>1</sup> 3d<sup>10</sup> for a fully filled d-subshell.

For ions, electrons are removed from the outermost shell first (e.g., Fe<sup>2+</sup> from Fe [Ar] 4s<sup>2</sup> 3d<sup>6</sup> becomes [Ar] 3d<sup>6</sup>). These rules predict chemical behavior, as valence electrons determine bonding.

## **2. Explain atomic and ionic radii and their variation in the periodic table.**

Atomic radius is the distance from the nucleus to the outermost electron shell, typically measured as half the internuclear distance in a homonuclear diatomic molecule (covalent radius) or in metals (metallic radius). Ionic radius is the effective size of an ion in a crystal lattice.

### **Variation Across a Period (Left to Right):**

- Atomic radius decreases due to increasing effective nuclear charge ( $Z_{\text{eff}}$ ). As atomic number increases, protons pull electrons closer, with poor shielding by electrons in the same shell. For example, in period 3, Na (186 pm) > Mg (160 pm) > Al (143 pm) > Si (117 pm) > P (110 pm) > S (104 pm) > Cl (99 pm) > Ar (98 pm).
- Ionic radii: Cations are smaller than neutral atoms (e.g., Na<sup>+</sup> 102 pm < Na 186 pm) due to electron loss and increased  $Z_{\text{eff}}$ . Anions are larger (e.g., Cl<sup>-</sup> 181 pm > Cl 99 pm) due to electron addition and repulsion.

### **Variation Down a Group (Top to Bottom):**

- Atomic radius increases as new shells are added, outweighing the increase in  $Z_{\text{eff}}$  due to shielding by inner electrons. For example, in group 1: Li (152 pm) < Na (186 pm) < K (231 pm) < Rb (244 pm) < Cs (262 pm).
- Ionic radii follow similar trends: Larger down the group for both cations and anions due to additional shells.

Exceptions: In d-block, radii decrease slightly across due to poor d-orbital shielding (lanthanide contraction in f-block causes even smaller changes). For isoelectronic species (same electrons), radius decreases with increasing Z (e.g., O<sup>2-</sup> > F<sup>-</sup> > Ne > Na<sup>+</sup> > Mg<sup>2+</sup>), as higher nuclear charge pulls electrons tighter.

These variations influence properties like density and reactivity.

## **4. Define ionization energy and explain the factors affecting it.**

Ionization energy (IE) is the minimum energy required to remove an electron from a gaseous atom or ion in its ground state, forming a cation. It is measured in kJ/mol or eV. First IE removes the first electron, second IE the next, and so on; successive IEs increase as removing electrons from cations is harder.

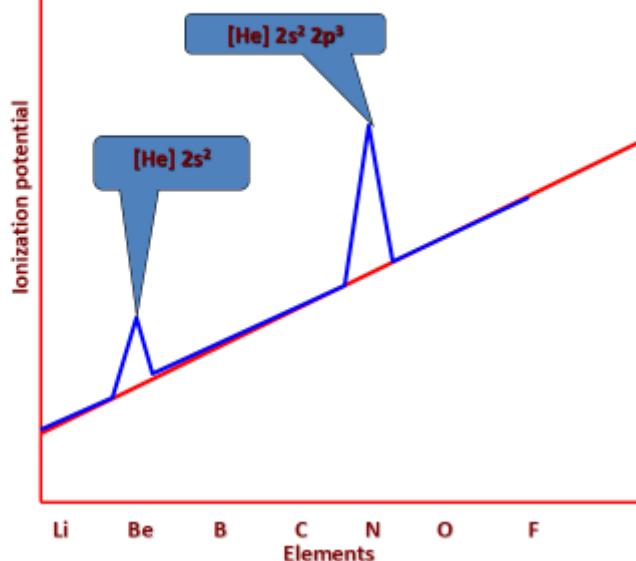
## Factors Affecting Ionization Energy:

1. **Atomic Radius:** Larger radius means electrons are farther from the nucleus, easier to remove, so lower IE. Down a group, IE decreases as radius increases.
2. **Effective Nuclear Charge ( $Z_{\text{eff}}$ ):** Higher  $Z_{\text{eff}}$  (more protons with poor shielding) holds electrons tighter, increasing IE. Across a period, IE generally increases due to rising  $Z_{\text{eff}}$ .
3. **Electron Configuration:** Half-filled or fully filled subshells are stable, leading to higher IE. For example, Nitrogen ( $1s^2 2s^2 2p^3$ ) has higher IE than Oxygen ( $1s^2 2s^2 2p^4$ ) because N has half-filled p-orbitals, while O's paired electron is easier to remove.
4. **Shielding Effect:** Inner electrons shield outer ones from nuclear pull, reducing  $Z_{\text{eff}}$  and IE. Poor shielding in the same shell increases IE across periods.
5. **Penetration Effect:** s-electrons penetrate closer to the nucleus than p or d, making them harder to remove if valence.

Trends: Across a period, IE increases with exceptions (e.g., group 2 to 13 drop due to  $s^2$  to  $p^1$  transition; group 15 to 16 drop due to half-filled stability). Down a group, IE decreases. Alkali metals have low IE (easy to form  $+1$  ions), noble gases high (stable configuration).

IE influences metallic character: Low IE means more metallic, easier cation formation.

The first ionization energies increase along the period and decrease down the group.



## 5. Define electron affinity and explain its variation and exceptions.

Electron affinity (EA) is the energy change when an electron is added to a neutral gaseous atom in its ground state, forming an anion. It is typically exothermic (negative value) for most elements, releasing energy, but endothermic (positive) for some. Measured in kJ/mol, higher magnitude means greater tendency to gain electrons.

## Variation in the Periodic Table:

- **Across a Period:** EA generally becomes more negative (increases in magnitude) from left to right due to increasing  $Z_{\text{eff}}$  and decreasing radius, making it easier to add an electron to a smaller, more charged nucleus. Halogens have the most negative EA (e.g., Cl -349 kJ/mol), as they need one electron for stable octet.
- **Down a Group:** EA becomes less negative (decreases in magnitude) as atomic size increases, and the added electron experiences more repulsion from larger electron cloud and better shielding.

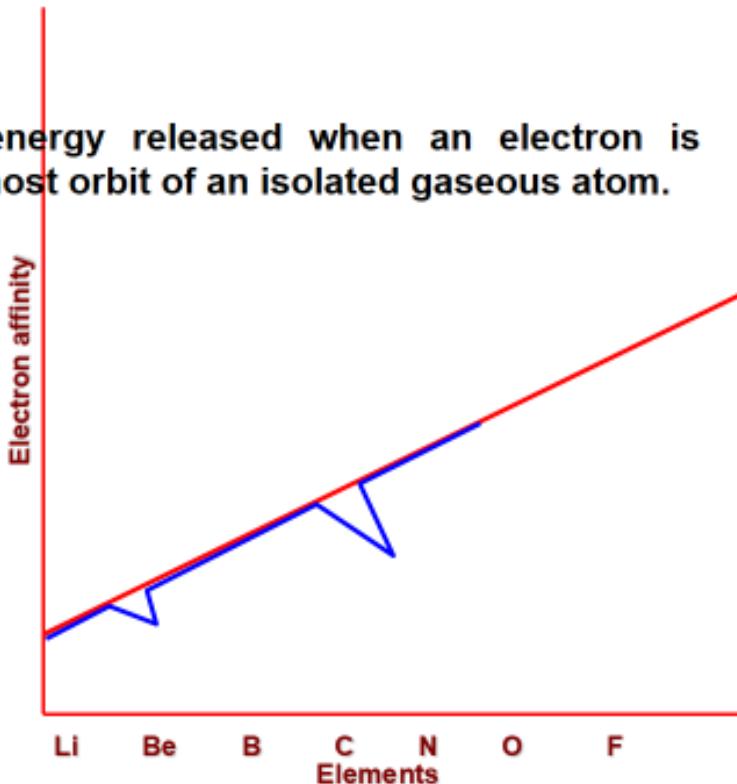
**Exceptions:**

- Group 2 (Be, Mg) and 18 (noble gases) have positive or near-zero EA because their stable  $s^2$  or fully filled configurations resist addition (e.g., Ne +21 kJ/mol).
- Nitrogen and group 15 have less negative EA than expected due to half-filled p-orbitals; adding an electron pairs it, causing repulsion (N -7 kJ/mol vs. O -141 kJ/mol).
- Fluorine has less negative EA (-328 kJ/mol) than Chlorine (-349 kJ/mol) due to small size and high electron density in F, leading to greater repulsion for the added electron.
- Second EA is always positive (endothermic) as adding to an anion requires overcoming repulsion.

EA influences non-metallic character: High EA means stronger oxidizing agents, like halogens forming anions easily.

**Electron affinity:**

**Amount of energy released when an electron is added to the outermost orbit of an isolated gaseous atom.**



**6. Explain electronegativity and describe its influence on bond formation.**

Electronegativity (EN) is the tendency of an atom in a molecule to attract shared electrons towards itself. It is a dimensionless quantity, with Pauling scale being common ( $F = 4.0$ ,  $C_s = 0.7$ ). Mulliken defines it as  $(IE + EA)/2$ , linking to ionization energy and electron affinity.

**Variation:** EN increases across a period (higher Z<sub>eff</sub> pulls electrons) and decreases down a group (larger size reduces pull). Non-metals have high EN, metals low.

### Influence on Bond Formation:

- **Ionic Bonds:** Large EN difference ( $>1.7$  on Pauling scale) leads to electron transfer, forming ions (e.g., NaCl, EN diff. 2.1; Na (0.9) transfers to Cl (3.0)).
- **Covalent Bonds:** Small EN difference ( $<0.5$ ) means equal sharing (non-polar, e.g., H<sub>2</sub>, EN diff. 0).
- **Polar Covalent Bonds:** Moderate difference (0.5-1.7) causes unequal sharing, creating dipoles (e.g., HCl, EN diff. 0.9; partial charges  $\delta+$  on H,  $\delta-$  on Cl).
- EN determines bond polarity, affecting solubility, boiling points, and reactivity. High EN elements like O, N form hydrogen bonds. In molecules, EN guides geometry and acid-base behavior (e.g., higher EN makes acids stronger).

EN is relative and varies with hybridization/oxidation state, but it's crucial for predicting chemical bonds.

## 7. Write a note on lanthanide contraction and its consequences.

Lanthanide contraction refers to the gradual decrease in atomic and ionic radii across the lanthanide series (Ce to Lu), despite increasing atomic number. This occurs because the 4f electrons are poorly shielding; as protons increase,  $Z_{eff}$  rises, pulling electrons closer. The contraction is about 20 pm for atoms and more pronounced for +3 ions (e.g., La<sup>3+</sup> 103 pm to Lu<sup>3+</sup> 86 pm).

### Consequences:

1. **Similar Properties:** Lanthanides have very similar chemical properties due to comparable sizes and +3 oxidation states, making separation difficult (e.g., via ion exchange).
2. **Impact on d-block:** Post-lanthanide elements (e.g., Hf) have radii similar to Zr (above them) due to contraction, leading to "twin" properties in 4d and 5d series (e.g., Zr-Hf hard to separate).
3. **Density Increase:** Smaller sizes increase density across the series.
4. **Basicity Decrease:** Ln<sup>3+</sup> ions become less basic from La to Lu as smaller size increases charge density, strengthening Ln-OH bonds.
5. **Complex Formation:** Smaller ions form more stable complexes towards the end.
6. Analogous actinide contraction exists but is less due to 5f orbital extension.

This phenomenon affects periodic trends and applications in magnets, catalysts, and phosphors.

## 8. Discuss the periodic trends in atomic size, ionization energy, electron affinity, and electronegativity.

Periodic trends arise from variations in atomic structure across the table.

- **Atomic Size (Radius):** Decreases across a period due to increasing Z<sub>eff</sub> compressing shells; increases down a group as new shells add distance. Example: Period 2: Li (152 pm) > Be (111 pm) > B (85 pm) > C (77 pm) > N (75 pm) > O (73 pm) > F (72 pm). Group 17: F (72 pm) < Cl (99 pm) < Br (114 pm) < I (133 pm).
- **Ionization Energy (IE):** Increases across a period (higher Z<sub>eff</sub> holds electrons tighter) with exceptions (e.g., drops at group 13, 16 due to subshell stability); decreases down a group (larger size, better shielding). Example: Period 3: Na (496 kJ/mol) < Mg (738) < Al (577, drop) < Si (786) < P (1012) < S (1000, slight drop) < Cl (1251) < Ar (1520). Group 1: Li (520) > Na (496) > K (419).
- **Electron Affinity (EA):** Becomes more negative across a period (easier to add electron to higher Z<sub>eff</sub>); less negative down a group (larger size increases repulsion). Exceptions: Noble gases positive; F less than Cl. Example: Group 17: F (-328 kJ/mol) > Cl (-349) > Br (-325) > I (-295).
- **Electronegativity (EN):** Increases across a period, decreases down a group, mirroring IE and EA. Example: Period 2: Li (1.0) < Be (1.5) < B (2.0) < C (2.5) < N (3.0) < O (3.5) < F (4.0). Group 1: Li (1.0) > Na (0.9) > K (0.8).

These trends predict reactivity: Left/bottom more metallic (low IE, EN), right/top more non-metallic (high IE, EA, EN).

## 9. Explain the stability of half-filled and completely filled orbitals.

Half-filled and completely filled orbitals exhibit extra stability due to quantum mechanical factors, influencing electron configurations and properties.

- **Completely Filled Orbitals:** A subshell with all orbitals occupied (e.g., s<sup>2</sup>, p<sup>6</sup>, d<sup>10</sup>) has paired electrons, minimizing energy via symmetry and exchange energy. Noble gases (ns<sup>2</sup> np<sup>6</sup>) are inert due to this stability, with high IE.
- **Half-Filled Orbitals:** Subshells like p<sup>3</sup>, d<sup>5</sup>, f<sup>7</sup> have one electron per orbital with parallel spins (Hund's rule), maximizing exchange energy (stabilizing interactions between same-spin electrons) and reducing repulsion. This lowers overall energy.

Examples:

- Nitrogen (2s<sup>2</sup> 2p<sup>3</sup>): Half-filled p, higher IE than Oxygen (2s<sup>2</sup> 2p<sup>4</sup>).
- Chromium (4s<sup>1</sup> 3d<sup>5</sup>): Deviates from expected 4s<sup>2</sup> 3d<sup>4</sup> for half-filled d and s.
- Manganese (4s<sup>2</sup> 3d<sup>5</sup>): Stable half-filled d, prefers +2 oxidation but shows higher states.
- Copper (4s<sup>1</sup> 3d<sup>10</sup>): Fully filled d for stability.

Consequences: Anomalous configurations (e.g., Nb, Pd), higher IE/EA at these points, and preference for oxidation states retaining such stability (e.g., Mn<sup>2+</sup> 3d<sup>5</sup>).

This stability explains exceptions in trends and reactivity.

## 10. Describe the variation of ionization energy across a period and down a group.

Ionization energy (IE) is the energy to remove an electron from a gaseous atom.

### Across a Period (Left to Right):

- IE generally increases due to decreasing atomic radius and increasing  $Z_{\text{eff}}$ ; electrons are held tighter.
- Exceptions:
  - Group 2 to 13: Drop (e.g., Be 899 kJ/mol > B 801) as removing from  $p^1$  is easier than  $s^2$ .
  - Group 15 to 16: Drop (e.g., N 1402 > O 1314) due to half-filled  $p^3$  stability in N.
  - Transition metals: Slight increase, but variable due to d-orbitals. Example (Period 2): Li (520) < Be (899) < B (801) < C (1086) < N (1402) < O (1314) < F (1681) < Ne (2081).

### **Down a Group (Top to Bottom):**

- IE decreases as atomic radius increases (electrons farther, weaker attraction) and shielding improves, reducing  $Z_{\text{eff}}$  on valence electrons.
- Exceptions minor, like slight anomalies in d-block due to contraction. Example (Group 1): Li (520) > Na (496) > K (419) > Rb (403) > Cs (376). Example (Group 17): F (1681) > Cl (1251) > Br (1140) > I (1008).

These variations reflect metallic character increasing down/left, as low IE facilitates cation formation.

## **11. Explain the factors responsible for periodicity in the properties of elements.**

Periodicity arises from repeating patterns in electron configurations as atomic number increases, governed by quantum mechanics.

### **Key Factors:**

1. **Atomic Number and Electron Configuration:** Properties repeat when similar valence configurations occur (e.g., group 1:  $ns^1$ , all alkali metals).
2. **Principal Quantum Number ( $n$ ):** New periods start with new shells, increasing size down groups.
3. **Effective Nuclear Charge ( $Z_{\text{eff}}$ ):** Increases across periods, compressing atoms and altering properties like IE, EN.
4. **Shielding Effect:** Inner electrons reduce  $Z_{\text{eff}}$  on outer ones; poor in same shell (period trend), better in inner shells (group trend).
5. **Orbital Types:** s, p, d, f blocks show distinct behaviors due to orbital shapes and penetration.
6. **Subshell Stability:** Half/fully filled orbitals cause exceptions, affecting IE, EA.

These lead to periodic trends in size, IE, EA, EN, valence, reactivity (e.g., metals left, non-metals right). Mendeleev's table captured this empirically; modern understanding ties it to atomic structure.

## **12. Write short notes on isoelectronic species and their trends in ionic radii.**

Isoelectronic species are atoms/ions with the same number of electrons but different nuclear charges ( $Z$ ). Examples:  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Ne}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  (all 10 electrons).

### Trends in Ionic Radii:

- Radius decreases as  $Z$  increases, since higher nuclear charge pulls the same electron cloud tighter.
- Example:  $O^{2-}$  (140 pm) >  $F^-$  (133 pm) > Ne (neutral, but effective ~100 pm) >  $Na^+$  (102 pm) >  $Mg^{2+}$  (72 pm) >  $Al^{3+}$  (53.5 pm).
- Anions larger than cations for same electrons due to lower  $Z$  (less pull, more repulsion in anions).
- Influences properties: Smaller ions have higher charge density, stronger lattices (e.g., MgO higher melting point than NaF).
- In periodic table, isoelectronic series show decreasing size across periods.

This trend explains why cations are smaller than parent atoms, anions larger.

### 13. Explain the relationship between effective nuclear charge and atomic properties.

Effective nuclear charge ( $Z_{eff}$ ) is the net positive charge experienced by valence electrons, calculated as  $Z_{eff} = Z - \sigma$  ( $Z$  = atomic number,  $\sigma$  = shielding constant). It increases across periods ( $\sigma < Z$  increase) and slightly down groups.

### Relationship to Atomic Properties:

- Atomic Radius:** Higher  $Z_{eff}$  decreases radius by pulling electrons closer (period trend: decrease; group: increase as  $\sigma$  rises more).
- Ionization Energy:** Higher  $Z_{eff}$  increases IE, harder to remove electrons (increases across periods, decreases down groups).
- Electron Affinity:** Higher  $Z_{eff}$  makes EA more negative, easier to add electrons (increases across periods).
- Electronegativity:** Correlates positively with  $Z_{eff}$ , stronger pull on shared electrons.
- Reactivity:** Low  $Z_{eff}$  in metals (easy electron loss); high in non-metals (electron gain).

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### 2 MARK QUESTIONS

#### 1. State Mendeleev's periodic law.

Mendeleev's periodic law, proposed by Dmitri Mendeleev in 1869, states that the properties of elements are periodic functions of their atomic weights. This means that when elements are arranged in order of increasing atomic mass, their physical and chemical properties repeat at regular intervals. Mendeleev used this principle to create the first comprehensive periodic table, where he grouped elements with similar properties into columns (groups) and rows (periods). He even left gaps for undiscovered elements and predicted their properties based on the patterns, such as for gallium (eka-aluminum) and germanium (eka-silicon). This law was empirical and focused on atomic mass, but it had limitations, such as anomalies in placement

(e.g., tellurium before iodine despite higher mass), which were later resolved by the modern periodic law.

## **2. State modern periodic law and name the scientist who proposed it.**

The modern periodic law states that the physical and chemical properties of elements are periodic functions of their atomic numbers. This law emphasizes that the arrangement of elements should be based on the number of protons in the nucleus (atomic number) rather than atomic mass, ensuring that elements with similar electron configurations fall into the same group, leading to periodic repetition of properties. It was proposed by Henry Gwyn Jeffreys Moseley in 1913, based on his X-ray spectroscopy experiments, which showed that the square root of X-ray frequencies is proportional to atomic number, resolving inconsistencies in Mendeleev's table (e.g., correct placement of argon before potassium and cobalt before nickel).

## **3. Define atomic radius.**

Atomic radius is defined as the distance from the center of the nucleus to the outermost electron shell or the boundary of the electron cloud in an atom. It represents the size of the atom and is typically measured in picometers (pm). Since atoms do not have a sharp boundary, atomic radius is often determined empirically: for non-metals, it's half the internuclear distance in a homonuclear diatomic molecule (covalent radius); for metals, it's half the distance between adjacent atoms in a metallic lattice (metallic radius). Atomic radius influences many properties, such as density, reactivity, and bonding behavior, and varies periodically across the table due to changes in effective nuclear charge and electron shielding.

## **4. Define covalent radius.**

Covalent radius is defined as half the internuclear distance between two identical atoms that are bonded together by a single covalent bond in a molecule. It is a measure of the atomic size in the context of covalent bonding and is commonly used for non-metallic elements. For example, the covalent radius of carbon is half the C-C bond length in diamond or ethane (approximately 77 pm). This value helps in calculating bond lengths in molecules and understanding molecular geometry. Covalent radii are smaller than van der Waals radii because they involve shared electrons in a bond, pulling atoms closer together compared to non-bonded interactions.

## **5. What is van der Waals radius?**

The van der Waals radius is defined as half the shortest internuclear distance between two non-bonded atoms that are in close contact but not chemically bonded, such as in a molecular crystal or between atoms in adjacent molecules. It represents the effective size of an atom when considering weak intermolecular forces (van der Waals forces) and is larger than the covalent or ionic radius because it accounts for the electron cloud's extent in non-bonding situations. For example, the van der Waals radius of hydrogen is about 120 pm, compared to its covalent radius of 37 pm. This radius is useful in predicting molecular packing, steric effects, and the volume occupied by atoms in gases or solids, and it's often measured for noble gases or in crystal structures.

## **6. Define ionic radius.**

Ionic radius is defined as the effective distance from the nucleus to the outermost electron shell of an ion in an ionic compound, typically measured in a crystal lattice. It accounts for the size of cations (positively charged ions, which are smaller than neutral atoms due to electron loss and increased nuclear pull) or anions (negatively charged ions, which are larger due to electron addition and increased repulsion). For example, the ionic radius of  $\text{Na}^+$  is 102 pm, while  $\text{Cl}^-$  is 181 pm. Ionic radii are determined from X-ray crystallography data and are crucial for understanding ionic bond strengths, lattice energies, and solubility. They vary with coordination number (number of surrounding ions) and follow periodic trends similar to atomic radii.

## 7. What are isoelectronic species? Give one example.

Isoelectronic species are atoms, ions, or molecules that have the same number of electrons and thus the same electron configuration, but differ in the number of protons (nuclear charge). This leads to differences in size and properties despite identical electron counts. For example, in a series like  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Ne}$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$ , all have 10 electrons (configuration:  $1s^2\ 2s^2\ 2p^6$ ), but their sizes decrease as nuclear charge increases ( $\text{O}^{2-}$  largest,  $\text{Mg}^{2+}$  smallest) due to stronger attraction pulling the electron cloud tighter. Isoelectronic comparisons help explain trends in ionic radii, ionization energies, and chemical behavior, such as why  $\text{Mg}^{2+}$  forms stronger lattices than  $\text{Na}^+$ .

## 8. State Hund's rule.

Hund's rule, also known as the rule of maximum multiplicity, states that when electrons are added to degenerate orbitals (orbitals of equal energy, such as the three p-orbitals or five d-orbitals), they will occupy each orbital singly with parallel spins before any orbital is doubly occupied. This configuration minimizes electron-electron repulsion and maximizes the total spin multiplicity, leading to a lower energy state. For example, in the carbon atom ( $1s^2\ 2s^2\ 2p^2$ ), the two p-electrons occupy separate p-orbitals with parallel spins ( $\uparrow\uparrow$ ) rather than pairing in one orbital. This rule is part of the principles governing electron configurations and explains magnetic properties (paramagnetism in unpaired electrons) and exceptions in periodic trends.

## 9. State Pauli's exclusion principle.

Pauli's exclusion principle, proposed by Wolfgang Pauli in 1925, states that no two electrons in an atom can have the same set of four quantum numbers ( $n$ : principal,  $l$ : azimuthal,  $m_l$ : magnetic,  $m_s$ : spin). This implies that each orbital can hold a maximum of two electrons, which must have opposite spins ( $m_s = +1/2$  and  $-1/2$ ). The principle arises from the fermionic nature of electrons and quantum mechanics, preventing electrons from occupying the same quantum state. For example, the 1s orbital can have two electrons: one with spin up and one with spin down. This rule is fundamental to electron configurations, the structure of the periodic table, and the stability of matter, as it forces electrons into higher energy levels, creating shells and subshells.

## 10. State Aufbau principle.

The Aufbau principle, from the German word for "building up," states that electrons in an atom fill atomic orbitals in order of increasing energy levels, starting from the lowest available orbital. The sequence is determined by the  $(n + l)$  rule:  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p <$

$5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$ . For example, potassium's configuration is  $[\text{Ar}] 4s^1$ , filling 4s before 3d. Exceptions occur for stability, like in chromium ( $[\text{Ar}] 4s^1 3d^5$ ). This principle, combined with Pauli and Hund rules, predicts electron configurations, which determine an element's chemical properties and placement in the periodic table.

## 11. Write the $(n + l)$ rule.

The  $(n + l)$  rule is used to determine the order in which atomic orbitals are filled with electrons according to the Aufbau principle. It states that orbitals are filled in order of increasing  $(n + l)$  value, where  $n$  is the principal quantum number (shell) and  $l$  is the azimuthal quantum number (subshell:  $s=0$ ,  $p=1$ ,  $d=2$ ,  $f=3$ ). If two orbitals have the same  $(n + l)$  value, the one with the lower  $n$  is filled first. For example:

- 1s:  $n=1, l=0, n+l=1$
- 2s:  $n=2, l=0, n+l=2$
- 2p:  $n=2, l=1, n+l=3$
- 3s:  $n=3, l=0, n+l=3$  (but lower  $n$  than 2p? Wait, 3s follows 2p because after 2p (3), next is 3s (3), but 2p has lower  $n$  so actually rule is: same sum, lower  $n$  first—but in sequence, 2p ( $n=2$ , sum=3) before 3s ( $n=3$ , sum=3), yes, lower  $n$ .)
- 4s ( $n=4, l=0, \text{sum}=4$ ) before 3d ( $n=3, l=2, \text{sum}=5$ ). This rule ensures the lowest energy configuration and explains the orbital filling order in multi-electron atoms.

## 12. What are s-, p-, d-, and f-block elements?

s-, p-, d-, and f-block elements are classifications in the periodic table based on the type of orbital being filled by their valence electrons:

- **s-block elements:** Valence electrons in s-orbitals (capacity: 2). Includes groups 1 (alkali metals, e.g., Na:  $[\text{Ne}] 3s^1$ , highly reactive) and 2 (alkaline earth metals, e.g., Ca:  $[\text{Ar}] 4s^2$ ), plus H and He. They form  $+1/+2$  cations easily.
- **p-block elements:** Valence electrons in p-orbitals (capacity: 6). Groups 13-18, diverse: metals (e.g., Al:  $[\text{Ne}] 3s^2 3p^1$ ), non-metals (e.g., O:  $[\text{He}] 2s^2 2p^4$ ), metalloids (e.g., Si), and noble gases (e.g., Ne:  $[\text{He}] 2s^2 2p^6$ , inert).
- **d-block elements:** Valence electrons in d-orbitals (capacity: 10). Groups 3-12, transition metals (e.g., Fe:  $[\text{Ar}] 4s^2 3d^6$ ), with variable oxidation states, colored compounds, and catalytic properties due to partially filled d-orbitals.
- **f-block elements:** Valence electrons in f-orbitals (capacity: 14). Lanthanides (Ce-Lu, e.g., Ce:  $[\text{Xe}] 6s^2 4f^1 5d^1$ ) and actinides (Th-Lr, e.g., U:  $[\text{Rn}] 7s^2 5f^3 6d^1$ ), inner transition metals with similar properties (+3 states common), often radioactive.

This blocking reflects electron configuration and influences reactivity, magnetism, and applications.

## 13. Define ionization energy.

Ionization energy (IE) is defined as the minimum amount of energy required to remove the most loosely bound electron from a neutral gaseous atom or ion in its ground state, forming a positively charged ion. It is expressed in kJ/mol or eV/atom. The first IE removes one electron (e.g.,  $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ ), second IE the next ( $\text{Na}^+ \rightarrow \text{Na}^{2+} + \text{e}^-$ ), with successive IEs increasing. IE measures how tightly electrons are held and depends on atomic structure. High IE indicates

stability (e.g., noble gases), low IE indicates reactivity (e.g., alkali metals). It's key to understanding metallic character and periodic trends.

## 14. Define electron affinity.

Electron affinity (EA) is defined as the change in energy (usually released) when an electron is added to a neutral gaseous atom in its ground state to form a negatively charged ion. It is expressed in kJ/mol and is typically negative for exothermic processes (energy released, e.g.,  $\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$ , EA = -349 kJ/mol). Positive EA means endothermic (energy absorbed, e.g., noble gases). EA reflects an atom's tendency to gain electrons and is highest for halogens. It influences non-metallic character, oxidizing power, and bond formation, with trends affected by size and configuration.

## 15. Why is the second electron affinity of oxygen positive?

The second electron affinity of oxygen is positive because adding a second electron to the already negatively charged  $\text{O}^-$  ion ( $\text{O}^- + \text{e}^- \rightarrow \text{O}^{2-}$ ) requires overcoming significant electrostatic repulsion between the incoming electron and the existing negative charge on the ion. The first EA is negative (-141 kJ/mol) as the neutral oxygen atom gains stability by approaching a noble gas configuration, but the  $\text{O}^-$  ion has extra electron density in a small 2p subshell, leading to strong repulsion that outweighs the nuclear attraction. Thus, energy must be supplied, making the process endothermic (+744 kJ/mol). This is common for all elements forming multiply charged anions, explaining why  $\text{O}^{2-}$  is stable only in ionic compounds where lattice energy compensates.

## 16. Define electronegativity.

Electronegativity (EN) is defined as the relative tendency of an atom in a molecule to attract a shared pair of electrons towards itself in a covalent bond. It is a dimensionless scale, with the Pauling scale being the most common (ranging from ~0.7 for Cs to 4.0 for F). EN can also be calculated via Mulliken as  $(\text{IE} + \text{EA})/2$ . It increases with smaller size and higher effective nuclear charge, influencing bond polarity: high EN difference leads to ionic bonds, low to non-polar covalent, moderate to polar covalent. EN affects acidity, basicity, and reactivity (e.g., high EN elements like O form hydrogen bonds).

## 17. What is lanthanide contraction?

Lanthanide contraction is the phenomenon where there is a steady and greater-than-expected decrease in atomic and ionic radii across the lanthanide series from lanthanum (La, atomic radius 187 pm) to lutetium (Lu, 174 pm), despite the increase in atomic number. This contraction is about 13 pm for atoms and more pronounced for +3 ions (~17 pm). It results in lanthanides having very similar sizes and properties, making separation challenging. The effect extends to post-lanthanide elements, causing 5d series elements (e.g., Hf) to have radii similar to 4d counterparts (e.g., Zr), known as "lanthanide twins."

## 18. What is the cause of lanthanide contraction?

The cause of lanthanide contraction is the poor shielding effect of the 4f electrons. As atomic number increases across the lanthanides, electrons are added to the 4f subshell, which is buried

deep within the atom and has a diffuse, non-spherical shape, providing inefficient screening of the nuclear charge from the outer electrons. Consequently, the effective nuclear charge ( $Z_{\text{eff}}$ ) experienced by the valence electrons (5d and 6s) increases more significantly than expected, pulling the electron cloud closer to the nucleus and reducing atomic/ionic size. This outweighs the size increase from added electrons, leading to contraction. Relativistic effects in heavier elements also contribute slightly.

## 19. Mention any two factors affecting ionization energy.

Two factors affecting ionization energy (IE) are:

1. **Atomic Radius:** Smaller atomic radius leads to higher IE because the valence electrons are closer to the nucleus, experiencing stronger electrostatic attraction, making removal more difficult. For example, IE increases across a period as radius decreases.
2. **Effective Nuclear Charge ( $Z_{\text{eff}}$ ):** Higher  $Z_{\text{eff}}$  increases IE as the valence electrons are more tightly held by the greater net positive charge. This occurs with increasing protons and poor shielding, such as across periods.

Other factors include shielding, electron configuration, and penetration, but these two are primary.

## 20. How does atomic radius vary across a period and down a group?

Atomic radius varies as follows:

- **Across a Period (left to right):** Atomic radius decreases due to increasing effective nuclear charge ( $Z_{\text{eff}}$ ). As protons increase, electrons are added to the same shell, providing poor shielding, so the nucleus pulls the electron cloud tighter. For example, in period 3: Na (186 pm) > Si (117 pm) > Cl (99 pm). Exceptions occur in transition metals due to d-orbital filling.
- **Down a Group (top to bottom):** Atomic radius increases because new electron shells are added, increasing the distance from the nucleus, and inner electrons provide better shielding, reducing  $Z_{\text{eff}}$  on valence electrons. For example, group 1: Li (152 pm) < Na (186 pm) < Cs (262 pm).

These trends affect properties like IE and density.

## 21. What is the trend of electronegativity in the periodic table?

The trend of electronegativity (EN) in the periodic table is:

- **Across a Period (left to right):** EN increases due to decreasing atomic radius and increasing effective nuclear charge, making atoms better at attracting shared electrons. For example, period 2: Li (1.0) < C (2.5) < F (4.0). Metals have low EN, non-metals high.
- **Down a Group (top to bottom):** EN decreases as atomic radius increases and shielding improves, reducing the nuclear pull on shared electrons. For example, group 17: F (4.0) > Cl (3.0) > I (2.5).

Noble gases have undefined or low EN as they don't form bonds easily. EN trends mirror non-metallic character and influence bond types.

## 22. Why do Zr and Hf have almost the same atomic radii?

Zirconium (Zr, atomic radius 160 pm) and hafnium (Hf, 159 pm) have almost the same atomic radii due to the lanthanide contraction. Zr is in the 4d series (period 5), Hf in the 5d series (period 6). Normally, radius should increase down the group due to added shells, but the intervention of the lanthanide series (4f filling) causes a contraction: poor 4f shielding increases  $Z_{\text{eff}}$ , shrinking sizes. This offsets the expected expansion, making Hf's radius similar to Zr's. This "twin" effect extends to properties like density and reactivity, making Zr-Hf separation difficult, and is seen in other pairs like Nb-Ta.

## 23. Differentiate between atomic radius and ionic radius.

- **Atomic Radius:** Measures the size of a neutral atom, defined as the distance from the nucleus to the outermost electron shell. It's determined as covalent radius (for non-metals, half the bond length) or metallic radius (for metals, half the lattice distance). It applies to isolated atoms and decreases across periods, increases down groups.
- **Ionic Radius:** Measures the size of an ion (cation or anion) in an ionic compound, accounting for electron gain/loss. Cations are smaller than neutral atoms (e.g.,  $\text{Na}^+$  102 pm < Na 186 pm) due to fewer electrons and higher  $Z_{\text{eff}}$ ; anions are larger (e.g.,  $\text{Cl}^-$  181 pm > Cl 99 pm) due to added electrons and repulsion. Ionic radius depends on coordination number and follows similar periodic trends but is context-specific to crystals.

Atomic radius is for neutrals, ionic for charged species; both influence bonding and properties.

## 24. What are the factors affecting electron affinity?

Factors affecting electron affinity (EA) include:

1. **Atomic Size/Radius:** Smaller radius increases EA (more negative) as the added electron is closer to the nucleus, experiencing stronger attraction. Larger atoms have weaker pull due to distance and repulsion.
2. **Effective Nuclear Charge ( $Z_{\text{eff}}$ ):** Higher  $Z_{\text{eff}}$  increases EA by enhancing the nucleus's ability to attract the extra electron.
3. **Electron Configuration:** Stable half-filled or fully filled subshells decrease EA (less negative or positive) as adding disrupts stability (e.g., N with  $p^3$  has low EA vs. O with  $p^4$ ).
4. **Shielding Effect:** Better shielding reduces  $Z_{\text{eff}}$ , lowering EA.
5. **Subshell Type:** p-block elements have higher EA than s-block; anomalies like F < Cl due to small size causing repulsion in F.

These factors explain trends: EA more negative across periods, less down groups.

## 25. Define effective nuclear charge.

Effective nuclear charge ( $Z_{\text{eff}}$ ) is defined as the net positive charge experienced by the valence electrons in an atom, accounting for the attraction from the nucleus minus the repulsion from inner electrons (shielding). It is calculated as  $Z_{\text{eff}} = Z - \sigma$ , where  $Z$  is the atomic number (protons) and  $\sigma$  is the shielding constant (approximated by Slater's rules). For example, in Na ( $Z=11$ ), valence 3s electron experiences  $Z_{\text{eff}} \approx 2.2$  due to shielding by 10 inner electrons.  $Z_{\text{eff}}$  increases across periods (poor same-shell shielding) and slightly down groups, influencing properties like radius (higher  $Z_{\text{eff}}$  shrinks), IE (increases), EA (increases), and EN (increases). It's key to understanding multi-electron atom behavior beyond hydrogen

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