# PERIODIC CLASSIFICATION OF ELEMENTS

Detailed Chemistry Notes for JEE Advanced

Concepts • Periodic Trends • Exceptions • Comparisons • Practice

How to study this chapter
Understand the reason behind each trend. For JEE Advanced, always check electronic configuration, charge, shell, pairing, and the species being compared.

## Contents


- Historical development and modern periodic law
- Modern long-form table, periods, groups, blocks, and configurations
- Effective nuclear charge, shielding, and penetration
- Atomic and ionic radii
- Ionisation enthalpy and successive ionisation
- Electron gain enthalpy and electronegativity
- Metallic character, oxides, hydrides, and reactivity
- Diagonal relationship, inert-pair effect, and second-period anomalies
- JEE comparison strategy, solved examples, and practice set


Prepared for concept-based revision. Always cross-check your current exam syllabus and official updates.

# 1. Development of Periodic Classification

The periodic table organises elements so that elements with related properties appear in recurring patterns. The modern table is arranged by increasing atomic number, not atomic mass.

## Historical milestones

| Scientist / system | Main idea | Limitation / significance |
|---|---|---|
| Dobereiner's triads | Groups of three similar elements; middle atomic mass was approximately the mean of the other two. | Applied to only a limited number of elements. |
| Newlands' law of octaves | When arranged by increasing atomic mass, every eighth element showed similar properties. | Worked mainly for lighter elements; no provision for undiscovered elements. |
| Mendeleev's table | Periodic law based on atomic mass; left gaps and predicted properties of undiscovered elements. | Could not consistently explain isotope placement and certain anomalous pairs. |
| Moseley's work | Established atomic number as the fundamental basis of classification. | Provided the basis for the modern periodic table. |

## Modern periodic law

The physical and chemical properties of elements are periodic functions of their atomic numbers. As atomic number increases, valence-shell electronic configurations recur periodically, producing recurring chemical properties.

Why atomic number is fundamental
Atomic number determines nuclear charge and, for a neutral atom, the number of electrons. It fixes the electronic configuration, which is the main basis of chemical behaviour.

## Consequences

- Isotopes have the same atomic number and therefore occupy the same position.
- The anomalous order of some pairs by atomic mass is resolved by atomic number.
- Gaps in Mendeleev's table allowed predictions of undiscovered elements; later discoveries supported the periodic approach.

# 2. Structure of the Modern Periodic Table

The long-form periodic table contains 7 periods (horizontal rows) and 18 groups (vertical columns). Members of a group often have related valence-shell configurations, although trends can be modified by size, shielding, and inert-pair effects.

## Periods

| Period | Subshell filling | Number of elements | General end configuration |
|---|---|---|---|
| 1 | 1s | 2 | $1s^1$ to $1s^2$ |
| 2 | 2s, 2p | 8 | $2s^1$ to $2s^22p^6$ |
| 3 | 3s, 3p | 8 | $3s^1$ to $3s^23p^6$ |
| 4 | 4s, 3d, 4p | 18 | 4s / 3d / 4p filling |
| 5 | 5s, 4d, 5p | 18 | 5s / 4d / 5p filling |
| 6 | 6s, 4f, 5d, 6p | 32 | Includes lanthanoids |
| 7 | 7s, 5f, 6d, 7p | Up to 32 | Includes actinoids |

## Blocks

| Block | Differentiating electron enters | Usual groups | General features |
|---|---|---|---|
| s | ns | 1–2 (He is $1s^2$ but placed in group 18) | Electropositive metals; common +1 and +2 states. |
| p | np | 13–18 | Contains metals, metalloids, and non-metals. |
| d | (n−1)d | 3–12 | Variable oxidation states; many form complexes. |
| f | (n−2)f | Lanthanoids and actinoids | Inner-transition elements; related chemistry within each series. |

- Period number generally equals the highest principal quantum number (n) in the ground-state configuration.
- Groups 1 and 2 generally end in $ns^1$ and $ns^2$; groups 13–18 generally end in $ns^2np^1$ to $ns^2np^6$ (He is $1s^2$).
- Transition element: an atom has an incomplete d subshell, or can form a cation with an incomplete d subshell. Zn, Cd, and Hg are generally excluded because their atoms and common +2 ions are $d^{10}$.
- Representative elements are s- and p-block elements; f-block elements are inner-transition elements.

# 3. Electronic Basis of Periodicity

Periodic trends arise from the combined effects of nuclear charge, shielding, penetration, and electron–electron repulsion. These factors should be considered together.

## Effective nuclear charge (Zeff)

An outer electron experiences less than the full nuclear charge because other electrons partially shield it. A simplified relation is $Z_{eff} = Z - S$, where Z is nuclear charge and S is the shielding constant. Slater's rules give an approximate estimate of S; they are not an exact quantum-mechanical description.

## Shielding and penetration

| Concept | Meaning | Key consequence |
|---|---|---|
| Shielding | Reduction in nuclear attraction due to other electrons. | Inner-shell electrons shield outer electrons effectively; same-shell shielding is less effective. |
| Penetration | Ability of an orbital electron density to approach the nucleus. | For the same n: s > p > d > f. |
| Across a period | Z increases while added electrons enter the same principal shell. | Zeff generally increases; atomic radius tends to decrease. |
| Down a group | A new shell is added and shielding increases. | Atomic size generally increases. |

JEE checkpoint
For a comparison, write configurations first. Identify the shell and subshell, check pairing and half-filled/full-filled stability, and then compare effective nuclear attraction.

## Orbital energy

For a given principal shell in a multi-electron atom, penetration commonly leads to ns < np < nd < nf in energy. Across different principal shells, energy ordering depends on the atom and occupancy; do not assume one universal order.

# 4. Atomic and Ionic Radii

An atom has no sharp boundary. Therefore, radius is defined operationally using distances between nuclei in particular bonding or crystal environments.

| Radius type | Definition |
|---|---|
| Covalent radius | Half the internuclear distance between two identical atoms joined by a covalent bond. |
| Metallic radius | Half the distance between nearest-neighbour nuclei in a metallic crystal. |
| van der Waals radius | Half the closest distance between two non-bonded atoms of the same element. |
| Ionic radius | Effective radius assigned to an ion in a crystal; depends on coordination number and environment. |

## Periodic trends

- Across a period, atomic radius generally decreases because Zeff increases while electrons enter the same principal shell.
- Down a group, atomic radius generally increases because a new shell is added and shielding increases.
- Cations are smaller than their parent atoms: electron removal reduces repulsion and may remove the outer shell.
- Anions are larger than their parent atoms because adding electrons increases electron–electron repulsion.
- For the same element, a higher positive charge generally gives a smaller cation.
- In an isoelectronic series, radius decreases as nuclear charge increases.

## Isoelectronic series

| Series (all species have 10 e⁻) | Radius order, largest to smallest |
|---|---|
| $O^{2-}$, $F^-$, Ne, $Na^+$, $Mg^{2+}$, $Al^{3+}$ | $O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+}$ |
| Reason | Electron count is constant; increasing nuclear charge pulls the same electron cloud more strongly. |

Caution
Ionic radii depend on coordination number and crystal environment. Compare values using the same convention and similar conditions.

# 5. Ionisation Enthalpy (IE)

Ionisation enthalpy is the enthalpy required to remove an electron from an isolated gaseous atom or ion in its ground state. It is positive for an endothermic process.

## $M(g) \rightarrow M^+(g) + e^- ; \Delta_i H_1 > 0$

## Successive ionisation enthalpies

$M(g) \rightarrow M^+(g) + e^-$ is the first IE; $M^+(g) \rightarrow M^{2+}(g) + e^-$ is the second IE, and so on. For a given element, $IE_1 < IE_2 < IE_3$ ... because each successive electron is removed from a more positively charged species. A very large jump occurs after all valence electrons have been removed.

## Factors and trends

- Higher Zeff generally increases IE; larger atomic radius generally lowers IE.
- Greater penetration generally raises the energy required to remove an electron.
- Across a period, IE generally increases; down a group, it generally decreases.
- Stable half-filled and fully filled subshells can raise IE relative to neighbouring configurations.
- Pairing repulsion can make removal from a paired orbital easier than the simple trend predicts.

| Comparison | Observed relation | Reason |
|---|---|---|
| Be vs B | $IE_1$(Be) > $IE_1$(B) | B loses a 2p electron; Be has filled $2s^2$. The 2p electron is higher in energy and less penetrating. |
| N vs O | $IE_1$(N) > $IE_1$(O) | N has stable $2p^3$; O has a paired 2p electron, with extra repulsion. |
| Mg vs Al | $IE_1$(Mg) > $IE_1$(Al) | Al loses a higher-energy 3p electron; Mg has $3s^2$. |
| P vs S | $IE_1$(P) > $IE_1$(S) | P has half-filled $3p^3$; S has a paired electron. |

Successive IE clue
A huge jump between $IE_n$ and $IE_{n+1}$ indicates that n electrons were removed from the valence shell; the next electron belongs to a stable inner shell.

# 6. Electron Gain Enthalpy (EGE)

Electron gain enthalpy is the enthalpy change when an electron is added to an isolated gaseous atom to form a gaseous anion: $X(g) + e^- \rightarrow X^-(g)$. If energy is released, $\Delta_{eg}H$ is negative. More negative means more exothermic.

### Important patterns

- Halogens have strongly negative EGE because gaining one electron completes the valence shell.
- Cl has a more negative EGE than F. The compact 2p orbital of F causes greater repulsion for the incoming electron than the larger 3p orbital of Cl.
- S has a more negative EGE than O for the analogous reason.
- Noble gases generally have positive EGE because the incoming electron must enter a higher-energy shell or orbital.
- Group 2 ($ns^2$) and group 15 ($np^3$) elements often have less negative EGE than nearby elements due to relatively stable configurations.
- The second electron gain enthalpy of an anion is positive in the gas phase because an electron is added to a negatively charged species.

Sign-convention warning
Electron gain enthalpy is usually written as an enthalpy change (negative when energy is released). Some sources quote electron affinity as the positive magnitude of energy released. Check the convention before comparing signs.

### Key comparisons

| Comparison | Conclusion |
|---|---|
| Cl vs F | ΔegH(Cl) is more negative than ΔegH(F). |
| S vs O | ΔegH(S) is more negative than ΔegH(O). |
| First vs second EGE | Second addition to $X^-$ is endothermic in the gas phase. |

## 7. Electronegativity and Bond Polarity

Electronegativity is the tendency of an atom in a molecule to attract the shared electron pair towards itself. Unlike IE and EGE, it is not the enthalpy change of an isolated gaseous atom.

### Trends and factors

- Across a period, electronegativity generally increases; down a group, it generally decreases.
- Fluorine is the most electronegative element on the commonly used Pauling scale.
- Electronegativity depends on oxidation state, hybridisation, and molecular environment; it is not an immutable atomic constant.
- For carbon, electronegativity follows $sp > sp^2 > sp^3$ because greater s-character holds electron density closer to the nucleus.
- In a polar bond, the more electronegative atom attracts electron density and becomes δ−; the other becomes δ+.

### Do not confuse these quantities

| Quantity | Meaning |
|---|---|
| Ionisation enthalpy | Energy change for removing an electron from an isolated gaseous atom/ion. |
| Electron gain enthalpy | Enthalpy change when an isolated gaseous atom gains an electron. |
| Electronegativity | Relative tendency of a bonded atom to attract the shared electron pair. |

## 8. Metallic Character, Oxides, Hydrides, and Reactivity

Metallic character is the tendency to lose electrons and form cations. Non-metallic character is associated with gaining or sharing electrons.

- Metallic character generally decreases across a period and increases down a group.
- Non-metallic character generally increases across a period and decreases down a group.
- For alkali metals, reactivity generally increases down the group because the valence electron is removed more easily.

- For halogens, oxidising power generally decreases down the group; $F_2$ is the strongest oxidising halogen in aqueous chemistry.

## Nature of oxides

Across a period, oxides generally change from basic through amphoteric to acidic as metallic character decreases. The trend is clearest for main-group oxides in comparable oxidation states.

| Examples | Typical nature |
|---|---|
| $Na_2O$, MgO | Basic |
| $Al_2O_3$, BeO, ZnO | Amphoteric |
| $SiO_2$, $P_4O_{10}$, $SO_3$, $Cl_2O_7$ | Acidic |
| CO, NO, $N_2O$ | Neutral (common examples) |

## Hydrides

Thermal stability of many covalent hydrides decreases down a group as the E–H bond becomes weaker. Acidity trends need separate reasoning: bond polarity, bond strength, and stability of the conjugate base all matter. Do not infer acidity from bond strength alone.

## Oxidising and reducing behaviour

Periodic position gives a useful first prediction, but actual redox strength in solution depends on standard potentials, solvation, pH, and reaction conditions. Avoid treating metallic character as an exact synonym for reducing power in every medium.

# 9. Diagonal Relationship, Inert-Pair Effect, and Anomalies

## Diagonal relationship

Some second-period elements resemble the third-period element diagonally below them. The classic pairs are Li–Mg, Be–Al, and B–Si. Similar size, charge density, and electronegativity contribute to these similarities.

| Pair | Selected similarities |
|---|---|
| Li and Mg | Both form nitrides directly; their carbonates decompose on heating; some salts show related solubility patterns. |
| Be and Al | Oxides and hydroxides are amphoteric; halides show appreciable covalent character; both form complexes. |
| B and Si | Hard, largely covalent network-forming metalloids; acidic oxides; halides undergo hydrolysis. |

## Inert-pair effect

In heavier p-block elements, the $ns^2$ electron pair is less readily involved in bonding. Consequently, oxidation states two units below the group oxidation state often become more stable down groups 13–16. Relativistic effects and poor shielding by inner d- and f-electrons contribute.

| Group | Higher state | Lower state increasingly stabilised (examples) |
|---|---|---|
| 13 | +3 | +1: Tl(I) is often more stable than Tl(III). |
| 14 | +4 | +2: Pb(II) is often more stable than Pb(IV). |
| 15 | +5 | +3: Bi(III) is more stable than Bi(V) in many compounds. |
| 16 | +6 | +4 becomes more important for heavier members. |

## Second-period anomalies

- Small size, high charge density, high electronegativity, and absence of vacant d orbitals in the valence shell distinguish period-2 elements.
- Second-period elements form strong pπ–pπ multiple bonds more readily: C=C, C≡C, N≡N, and O=O.
- They cannot expand the octet in the classical textbook description; heavier congeners can form hypercoordinate species, but modern bonding is more nuanced than simple d-orbital expansion.

- Their small size and high charge density often lead to stronger hydration and different covalent/ionic character compared with heavier congeners.

# 10. JEE Advanced Comparison Strategy

Use this checklist whenever a question asks you to arrange species or explain an exception.

- Identify the property: radius, IE, EGE, electronegativity, metallic character, acidity, basicity, or stability.
- Write electronic configurations and identify the orbital involved.
- Check isoelectronicity. If electron counts are equal, greater nuclear charge generally means smaller radius.
- Compare effective nuclear charge and distance from nucleus; consider shell addition and shielding.
- Check pairing, half-filled/full-filled subshells, penetration, inert-pair effect, and chemical environment.
- Give a reason based on electronic structure rather than quoting a memorised order.

## Solved illustrations

Example 1. Increasing ionic radius: $Al^{3+}$, $Mg^{2+}$, $Na^{+}$, $F^{-}$, $O^{2-}$.
All have 10 electrons. Nuclear charge increases from O (8) to Al (13), so the radius decreases. Order: $Al^{3+} < Mg^{2+} < Na^{+} < F^{-} < O^{2-}$.

Example 2. Compare $IE_1$ of N and O.
N is $1s^2 2s^2 2p^3$, a half-filled p subshell. O is $1s^2 2s^2 2p^4$ and has a paired p electron. Extra pairing repulsion makes electron removal easier from O; therefore $IE_1(N) > IE_1(O)$.

Example 3. Why is ΔegH(Cl) more negative than ΔegH(F)?
The incoming electron experiences strong repulsion in compact F 2p orbitals. The larger Cl 3p orbital accommodates it with less repulsion; therefore electron addition is more exothermic for Cl.

Example 4. Why is Pb(II) stable relative to Pb(IV)?
The $6s^2$ pair is less readily involved in bonding in heavy Pb; the inert-pair effect stabilises the +2 state in many compounds.

# 11. JEE Advanced Practice Questions

Attempt the questions before reading the answer key. Assume isolated gaseous species unless stated otherwise.

Q1. Arrange in increasing size: $Al^{3+}$, $Mg^{2+}$, $Na^{+}$, $F^{-}$, $O^{2-}$.

Answer: All are isoelectronic (10 electrons). Increasing nuclear charge contracts the radius: $Al^{3+} < Mg^{2+} < Na^{+} < F^{-} < O^{2-}$.

Q2. Which has the highest first IE among B, Be, C, and N?

Answer: N. IE generally rises across period 2; the half-filled $2p^3$ configuration adds stability.

Q3. Explain why $IE_1(Mg) > IE_1(Al)$.

Answer: Al loses a 3p electron, which is higher in energy and less penetrating than Mg's 3s electron.

Q4. Which has more negative EGE, O or S?

Answer: S. The larger 3p orbital has less repulsion for the incoming electron than compact O 2p.

Q5. Describe the broad change in oxide character across period 3.

Answer: Basic $Na_2O$ and MgO; amphoteric $Al_2O_3$; acidic $SiO_2$ and oxides of P, S, and Cl.

Q6. Why is the second EGE of oxygen positive?

Answer: Adding an electron to $O^{-}$ requires overcoming repulsion from the negative ion.

Q7. Name the classic diagonal pairs.

Answer: Li–Mg, Be–Al, and B–Si.

Q8. Why does metallic character increase down group 1?

Answer: The valence electron is farther from the nucleus and more shielded, so it is easier to remove.

Q9. Explain the stability of Pb(II) relative to Pb(IV).

Answer: The inert-pair effect makes the $6s^2$ pair less available for bonding, stabilising +2.

Q10. Arrange $IE_1$ of Be, B, N, O in increasing order.

Answer: B < Be < O < N. The key exceptions are Be > B and N > O.

# 12. Rapid Revision Sheet

| Property | Across a period (general trend) | Down a group (general trend) |
|---|---|---|
| Atomic radius | Decreases | Increases |
| First ionisation enthalpy | Increases, with exceptions | Decreases |
| Electron gain enthalpy | Often becomes more negative towards halogens; exceptions occur | Often becomes less negative; irregular |
| Electronegativity | Increases | Decreases |
| Metallic character | Decreases | Increases |
| Non-metallic character | Increases | Decreases |
| Oxide character | Basic → amphoteric → acidic | Often more basic down metallic groups |

## Must-remember exceptions

- IE: Be > B; N > O; Mg > Al; P > S.
- EGE: Cl is more negative than F; S is more negative than O.
- Isoelectronic radius: greater nuclear charge means smaller radius.
- Cations are smaller than parent atoms; anions are larger.
- Inert-pair effect stabilises lower oxidation states down heavier p-block groups.
- Diagonal pairs: Li–Mg, Be–Al, B–Si.

Final JEE strategy
Periodic trends are patterns, not exception-free laws. In every comparison, identify the species, charge, electronic configuration, shell, and physical environment. A short electronic-configuration argument is often the fastest route to the correct answer.

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