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CH 04

Periodic Trends — Size, Ionisation & Electronegativity

04

Effective nuclear charge, atomic and ionic radii, ionisation enthalpy, electron gain enthalpy, electronegativity, the nature of oxides, diagonal relationships and the inert pair effect — with every famous exception explained, an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Explain trends in atomic and ionic radius using effective nuclear charge and shielding
- Order isoelectronic species by size
- Explain the ionisation-enthalpy exceptions (Be > B, N > O, Mg > Al, P > S) and identify a group from successive ionisation enthalpies
- Explain why Cl has a more negative electron gain enthalpy than F, and why noble gases are positive
- Predict the nature of oxides, diagonal relationships and the inert pair effect

INSIDE

A The big picture
B Effective nuclear charge
C Atomic radius
D Ionic radius
E Ionisation enthalpy
F Electron gain enthalpy

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Two ideas explain nearly every trend.

IN ONE LINE

Across a period effective nuclear charge rises, so atoms shrink and hold electrons more tightly; down a group new shells are added, so atoms grow and hold electrons less tightly. Half-filled and filled subshells explain the exceptions.

Property	Across a period (→)	Down a group (↓)
Atomic radius	Decreases	Increases
Ionisation enthalpy	Increases (with exceptions)	Decreases
Electron gain enthalpy	More negative	Less negative (with exceptions)
Electronegativity	Increases	Decreases
Metallic character	Decreases	Increases
Basic nature of oxides	Decreases (basic → acidic)	Increases

THINK OF IT LIKE THIS

Picture the nucleus as a magnet and the outer electrons as paper clips. Across a period the magnet gets stronger while the clips stay at about the same distance — they are pulled in closer and held tighter. Down a group the clips are placed on a new, outer ring and inner electrons get in the way — so the grip weakens.

SECTION B

Effective nuclear charge

B

The pull the outer electron actually feels.

$$Z_{eff} = Z - \sigma$$

Z = nuclear charge; σ = shielding (screening) constant from the other electrons

- Inner electrons shield the outer ones; electrons in the same shell shield each other only weakly.
- **Shielding power:** s > p > d > f. Poorly shielding d and f electrons explain the d-block and lanthanoid contractions.
- Across a period Z rises by 1 each step but σ rises by much less, so **Zeff increases**.
- Down a group Zeff on the outer electron changes only slightly, but the new shell is much farther out.

SECTION C

C

Atomic radius

How big is an atom?

- **Covalent radius:** half the distance between two bonded identical atoms (non-metals). **Metallic radius:** half the distance between neighbouring atoms in the metal lattice. **van der Waals radius:** half the distance between non-bonded atoms in neighbouring molecules — the largest of the three.
- **Across period 2:** Li (152 pm) > Be > B > C > N > O > F (64 pm). Noble gases are quoted as van der Waals radii, so they look larger than the halogen before them.
- **Down a group:** radius increases: Li < Na < K < Rb < Cs.

KEY IDEA

The Ga anomaly: Ga (135 pm) is slightly smaller than Al (143 pm). Ga follows the ten 3d elements, whose d electrons shield the extra nuclear charge poorly, so Ga's outer electrons feel a larger pull (the d-block contraction).

SECTION D

D

Ionic radius

Gaining or losing electrons changes size dramatically.

- **Cation < parent atom:** losing electrons (often a whole shell) leaves the same nuclear charge pulling fewer electrons. Na (186 pm) → Na^+ (102 pm).
- **Anion > parent atom:** extra electrons repel each other while nuclear charge is unchanged. Cl (99 pm) → Cl^- (181 pm).
- Higher positive charge → smaller: Fe^{3+} < Fe^{2+} < Fe.

KEY IDEA

Isoelectronic species (same number of electrons) — the one with more protons is smaller. For 10 electrons: N^{3-} (171) > O^{2-} (140) > F^- (133) > Na^+ (102) > Mg^{2+} (72) > Al^{3+} (54 pm).

SOLVED EXAMPLE 01 — **ISOELECTRONIC ORDERING**

Arrange S^{2-}, Cl^{-}, K^{+} and Ca^{2+} in increasing order of size.

SOLUTION

1. All have 18 electrons.
2. Protons: S 16, Cl 17, K 19, Ca 20.
3. More protons pull the same 18 electrons in more tightly.

ANSWER $Ca^{2+} < K^{+} < Cl^{-} < S^{2-}$.

CHECK YOURSELF

C1 Which is larger: Mg or Mg^{2+}? Why?

C2 Arrange O^{2-}, F^{-} and Na^{+} in decreasing size.

Answers at the end of the chapter.

SECTION E

Ionisation enthalpy

E

The energy needed to pull off the outermost electron.

$$M(g) \rightarrow M^{+}(g) + e^{-} \quad \Delta iH_1$$

Always positive (energy needed); second ΔiH_2 > first, because the electron leaves a positive ion

- **Across a period it increases** (higher Zeff, smaller atom). **Down a group it decreases** (larger atom, more shielding).
- Noble gases have the highest values in each period; alkali metals the lowest. He has the highest first ionisation enthalpy of all (2372 kJ mol^{-1}); Cs among the lowest.

Pair	Values (kJ mol^{-1})	Reason for the exception
Be > B	899 > 801	B loses a 2p electron, which is higher in energy and shielded by 2s
N > O	1402 > 1314	N has a stable half-filled $2p^3$; O loses a paired electron (repulsion helps)
Mg > Al	738 > 577	Al loses a 3p electron
P > S	1012 > 1000	P is half-filled $3p^3$

Successive ionisation enthalpies identify the group

A sudden very large jump appears when the next electron must come from a **filled inner shell**. The number of electrons removed before the jump = the number of valence electrons.

SOLVED EXAMPLE 02 — FINDING THE GROUP

An element has ΔiH_1 = 738, ΔiH_2 = 1451 and ΔiH_3 = 7733 kJ mol^{-1}. Which group is it in?

SOLUTION

1. $\Delta iH_2 \rightarrow \Delta iH_3$ is a five-fold jump; $\Delta iH_1 \rightarrow \Delta iH_2$ is only doubled.
2. So two electrons come off easily, and the third comes from the inner shell.

ANSWER Group 2 (these are the values for Mg).

SECTION F

Electron gain enthalpy

F

Energy change when a gaseous atom gains an electron.

$$X(g) + e^- \rightarrow X^-(g) \quad \Delta egH$$

Negative when energy is released; halogens have the most negative values

- Generally becomes **more negative across a period** and **less negative down a group**.
- **Noble gases:** positive — the electron would have to enter a new shell.
- **Be, Mg** (filled s^2) and **N** (half-filled p^3) have values near zero or positive.
- **Second electron gain enthalpy is always positive:** adding an electron to a negative ion needs energy ($O^- \rightarrow O^{2-}$ needs about +780 kJ mol^{-1}). O^{2-} exists in solids only because the lattice energy pays for it.

KEY IDEA

Cl is more negative than F (−349 vs −328 kJ mol^{-1}). F is so small that the incoming electron is crowded into the compact 2p subshell and repelled by the electrons already there. The same reason makes S more negative than O. Order for halogens: **Cl > F > Br > I**.

CHECK YOURSELF

C3 Why does neon have a positive electron gain enthalpy?

C4 Which has the more negative electron gain enthalpy: O or S?

Answers at the end of the chapter.

SECTION G

Electronegativity

G

How strongly a bonded atom pulls the shared pair toward itself.

- Not a property of an isolated atom — it describes an atom **in a bond**, so it has no unit. On the Pauling scale F = 4.0 (highest), O = 3.5, N = Cl = 3.0, C = 2.5, H = 2.1, Cs ≈ 0.7.

- Increases across a period, decreases down a group.
- A larger difference between two atoms → more polar bond; a difference above about 1.7 suggests largely ionic character.
- Electronegativity rises with oxidation state of the same element (Mn in $KMnO_4$ is far more electronegative than in MnO).

Ionisation enthalpy	Electron gain enthalpy	Electronegativity
Isolated gaseous atom	Isolated gaseous atom	Atom in a molecule
Measured (kJ mol^{-1})	Measured (kJ mol^{-1})	Relative scale, no unit

SECTION H

Oxides and metallic character

H

Metals on the left, non-metals on the right — and their oxides follow.

Period 3 oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Nature	Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Very strongly acidic

- **Amphoteric oxides** react with both acids and bases: BeO, Al_2O_3, ZnO, Ga_2O_3, SnO, SnO_2, PbO, PbO_2.
- **Neutral oxides:** CO, NO, N_2O.
- For one element, a higher oxidation state gives a more acidic oxide: MnO (basic) → Mn_2O_7 (acidic); CrO (basic) → Cr_2O_3 (amphoteric) → CrO_3 (acidic).
- **Metallic character** decreases across a period and increases down a group; reducing power of metals follows the same pattern.

SOLVED EXAMPLE 03 — AMPHOTERIC BEHAVIOUR

Show that Al_2O_3 is amphoteric.

SOLUTION

1. With acid: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ (acts as a base).
2. With alkali: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$ (acts as an acid).

ANSWER It reacts with both acids and bases.

SECTION I

Special behaviour

I

Second-period anomalies, diagonal pairs and the inert pair effect.

- **First member of each group is anomalous** (Li, Be, B, C, N, O, F): small size, high electronegativity, and no d orbitals. Its maximum covalency is 4 (B forms $[BF_4]^-$, Al forms $[AlF_6]^{3-}$). It forms pπ–pπ multiple bonds easily (C=C, N≡N, O=O) where heavier members prefer single bonds.
- **Diagonal relationship:** Li–Mg, Be–Al, B–Si resemble each other because their charge-to-radius ratios (and electronegativities) are similar. Example: Li and Mg both form nitrides on heating in N_2; BeO and Al_2O_3 are both amphoteric; B and Si both form acidic oxides and covalent hydrides.
- **Inert pair effect:** in groups 13–15, the ns^2 pair becomes more reluctant to take part in bonding down the group. So Tl^+ is more stable than Tl^{3+}, Pb^{2+} more stable than Pb^{4+} (PbO_2 is a strong oxidant), and Bi^{3+} more stable than Bi^{5+}.

KEY IDEA

Why the inert pair effect appears: the poor shielding by the 4f and 5d electrons pulls the 6s pair closer to the nucleus, making it harder to remove; the energy released by forming two extra bonds is not enough to pay for this.

SECTION J

Exam trap gallery

J

Where marks are lost in periodic trends.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
F has the most negative electron gain enthalpy.	Cl (−349) is more negative than F (−328 kJ mol^{-1}).
WHY F's small 2p subshell repels the incoming electron.	

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
O has a higher ionisation enthalpy than N.	N (1402) > O (1314 kJ mol^{-1}).
WHY N is half-filled $2p^3$; O loses a paired electron.	

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Al is smaller than Ga.	Ga (135 pm) is slightly smaller than Al (143 pm).
WHY Poor shielding by 3d electrons in Ga.	

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Electronegativity and electron gain enthalpy are the same thing.	$\Delta_{eg}H$ is for an isolated atom (kJ mol^{-1}); electronegativity is for a bonded atom (no unit).

WHY Different definitions, different scales.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Na^+ is larger than F^- because Na is larger than F.	F^- (133 pm) > Na^+ (102 pm).

WHY Isoelectronic: more protons → smaller.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
All second electron gain enthalpies are negative.	They are always positive.

WHY An electron is being added to a negative ion.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Pb^{4+} is more stable than Pb^{2+}, like C^{4+} chemistry.	Pb^{2+} is more stable (inert pair effect).

WHY The $6s^2$ pair resists bonding.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Al_2O_3 is basic because Al is a metal.	Al_2O_3 is amphoteric.

WHY It dissolves in both acid and alkali.

MEMORY HOOK

"**Left-down big, right-up tight**" — radius large at bottom-left; IE, EN high at top-right.

"**Be-B, N-O, Mg-Al, P-S**" — the four IE exceptions.

"**Chlorine wins the electron**" — most negative $\Delta_{eg}H$.

"**Li-Mg, Be-Al, B-Si go diagonal.**"

SECTION K

Practice MCQs

K

Levels: Easy, Moderate, Tough.

Q01 Atomic radius generally decreases across a period because: [EASY]

(a) shielding increases
(b) effective nuclear charge increases
(c) number of shells increases
(d) mass increases

Q02 The element with the highest electronegativity is: [EASY]

(a) O
(b) Cl
(c) F
(d) N

Q03 The smallest ion among these is: [EASY]

(a) Na^+
(b) Mg^{2+}
(c) Al^{3+}
(d) F^-

Q04 Which has a positive electron gain enthalpy? [EASY]

(a) Cl
(b) O
(c) Ne
(d) S

Q05 Which oxide is amphoteric? [EASY]

(a) Na_2O
(b) Al_2O_3
(c) SO_3
(d) P_4O_{10}

Q06 Correct order of first ionisation enthalpy: [MODERATE]

(a) B > Be
(b) O > N
(c) N > O
(d) Al > Mg

Q07 The most negative electron gain enthalpy is shown by: [MODERATE]

(a) F
(b) Cl
(c) Br
(d) I

Q08 Correct order of size: [MODERATE]

(a) $O^{2-} < F^- < Na^+$
(b) $Na^+ < F^- < O^{2-}$
(c) $F^- < O^{2-} < Na^+$
(d) $Na^+ < O^{2-} < F^-$

Q09 Ionisation enthalpies 496, 4562, 6910 kJ mol^{-1} suggest the element is in group: [MODERATE]

(a) 1
(b) 2
(c) 13
(d) 14

Q10 Diagonal relationship exists between: [MODERATE]

(a) Li and Na
(b) Be and Al
(c) B and Al
(d) Na and Mg

Q11 Maximum covalency of boron is 4 because: [MODERATE]

(a) it is small
(b) it has no d orbitals
(c) it is a metal
(d) it is electron-rich

Q12 Which pair has almost the same atomic radius? [MODERATE]

(a) Al and Ga
(b) Na and K
(c) B and Al
(d) Li and Be

Q13 The more stable oxidation state of thallium is: [TOUGH]

(a) +1
(b) +3
(c) +2
(d) +5

Q14 Second electron gain enthalpy of oxygen is: [TOUGH]

(a) negative
(b) positive
(c) zero
(d) equal to the first

Q15 Which is the most acidic oxide? [TOUGH]

(a) Na_2O
(b) MgO
(c) SiO_2
(d) Cl_2O_7

Answer key with explanations

Q01 **(b) effective nuclear charge increases** — Zeff rises.

Q02 **(c) F** — Pauling value 4.0.

Q03 **(c) Al^{3+}** — Isoelectronic; most protons.

Q04 **(c) Ne** — Noble gas.

Q05 **(b) Al_2O_3** — Reacts with acid and base.

Q06 **(c) N > O** — Half-filled $2p^3$.

Q07 **(b) Cl** — F is too small.

Q08 **(b) $Na^+ < F^- < O^{2-}$** — Fewer protons → larger.

Q09 **(a) 1** — Big jump after the first.

Q10 **(b) Be and Al** — Similar charge/radius ratio.

Q11 **(b) it has no d orbitals** — Only 2s and 2p available.

Q12 **(a) Al and Ga** — Ga 135, Al 143 pm.

Q13 **(a) +1** — Inert pair effect.

Q14 **(b) positive** — Adding e^- to O^-.

Q15 **(d) Cl_2O_7** — Cl in +7, far right.

Check-yourself answers

C1 Mg. Mg^{2+} has lost its whole 3s shell, and 12 protons pull 10 electrons.

C2 $O^{2-} > F^- > Na^+$.

C3 Its next electron would enter a new shell (3s), far from the nucleus and well shielded, so energy must be supplied.

C4 S (−200 vs −141 kJ mol^{-1}): O is small and its 2p subshell is crowded.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Zeff and size

- Zeff = Z − σ; rises across a period
- Radius: ↓ across, ↑ down
- Shielding s > p > d > f
- Ga (135) < Al (143) — d contraction

Ions

- Cation < atom < anion
- Isoelectronic: more protons → smaller
- $N^{3-} > O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$
- $Fe^{3+} < Fe^{2+}$

Ionisation enthalpy

- ↑ across, ↓ down; He highest
- Exceptions: Be > B, N > O, Mg > Al, P > S
- Big jump = inner shell reached
- $\Delta iH_2 > \Delta iH_1$ always

Electron gain enthalpy

- Cl > F > Br > I (most negative)
- S more negative than O
- Noble gases, Be, Mg, N ≈ 0 or +
- Second ΔegH always positive

Electronegativity and oxides

- F 4.0 > O 3.5 > N = Cl 3.0
- Na_2O basic → Al_2O_3 amphoteric → Cl_2O_7 acidic
- Amphoteric: BeO, Al_2O_3, ZnO, SnO, PbO
- Neutral: CO, NO, N_2O

Special behaviour

- 2nd-period: no d orbitals, max covalency 4
- Diagonal: Li–Mg, Be–Al, B–Si
- Inert pair: Tl^{+}, Pb^{2+}, Bi^{3+} stable
- PbO_2 strong oxidant

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