9701 CHEMISTRY · TOPIC 9 · AS LEVEL

Chemical Periodicity — Period 3

01 · ATOMIC AND IONIC RADIUS

Atomic radius falls across the period. Nuclear charge rises while electrons enter the same shell, so shielding is roughly constant and the outer electrons are pulled in more strongly.

Ionic radius drops sharply from Na^+ to Si^{4+} (cations lose a shell), then jumps at P^{3-} and falls again to Cl^- (anions gain electrons and repel).

02 · IONISATION ENERGY

Rises across the period — greater nuclear charge, smaller radius, similar shielding.

Two dips: Al < Mg because Al's electron leaves a higher-energy 3p; S < Pbecause S has a paired 3p electron and pair repulsion makes it easier to remove.

03 · MELTING POINT ACROSS PERIOD 3

Element	Structure	m.p.
Na → Al	giant metallic	rises
Si	giant covalent	highest
P_4, S_8, Cl_2	simple molecular	low
Ar	monatomic	lowest

Na → Al rises because the cations carry more charge and are smaller, so more delocalised electrons and stronger metallic bonding. Among the molecular elements, $S_8 > P_4 > Cl_2$ because the larger molecule has stronger London forces.

04 · REACTION WITH OXYGEN

Na burns with a yellow flame → Na_2O. Mg burns with a brilliant white flame → MgO. Al forms a protective oxide layer. Si, Pand S burn to SiO_2, P_4O_{10} and SO_2.

Oxidation number of the element in its highest oxide equals its group number.

05 · REACTION WITH WATER

Na — vigorous with cold water, floats and fizzes: $2Na + 2H_2O \rightarrow 2NaOH + H_2$, pH ~13.

Mg — very slow in cold water (pH ~10), but rapid with steam: $Mg + H_2O \rightarrow MgO + H_2$.

Al, Si — no reaction; Al is protected by its oxide layer.

06 · OXIDES

Oxide	Bonding	In water
Na_2O	ionic	pH 13, basic
MgO	ionic	pH 9, sparingly soluble
Al_2O_3	ionic w/ covalent character	insoluble, amphoteric
SiO_2	giant covalent	insoluble, weakly acidic
P_4O_{10}	simple covalent	pH 2, acidic
SO_2 / SO_3	simple covalent	pH 1–2, acidic

Basic → amphoteric → acidic across the period, tracking the change from metallic to non-metallic character.

07 · AMPHOTERIC AL_2O_3

As a base:
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

As an acid:
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

08 · ELECTRONEGATIVITY ACROSS PERIOD 3

Rises from Na to Cl — the nucleus is more highly charged and the atom smaller, so the shared pair is attracted more strongly.

This drives the change in bonding: Δχ with oxygen or chlorine falls across the period, so the compounds shift from ionic to covalent.

09 · EQUATIONS TO KNOW

$2Na + \frac{1}{2}O_2 \rightarrow Na_2O$
$2Mg + O_2 \rightarrow 2MgO$
$Si + O_2 \rightarrow SiO_2$
$P_4 + 5O_2 \rightarrow P_4O_{10}$
$S + O_2 \rightarrow SO_2$

$Na_2O + H_2O \rightarrow 2NaOH$
$MgO + H_2O \rightarrow Mg(OH)_2$
$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
$SO_3 + H_2O \rightarrow H_2SO_4$

10 · TRENDS AT A GLANCE

Property	Na → Ar
atomic radius	decreases
first IE	increases (dips at Al, S)
electronegativity	increases
melting point	peaks at Si
conductivity	high Na–Al, then none
oxide character	basic → amphoteric → acidic

All of it follows from two things: rising nuclear charge across the period, and the change in structure from giant metallic through giant covalent to simple molecular.

11 · WORKED EXAMPLE — EXPLAINING THE MELTING POINTS

Why does Al melt higher than Na?
Al^{3+} is smaller and carries three times the charge, and each atom releases three delocalised electrons, so the metallic bonding is much stronger.

Why does Si melt highest?
Giant covalent — melting breaks strong covalent bonds throughout the lattice.

Why is S_8 higher than P_4?
More electrons per molecule, so stronger London forces.

12 · IONIC RADII ACROSS PERIOD 3

Ion	Charge	Size
Na^+, Mg^{2+}, Al^{3+}	+1 → +3	falls sharply
P^{3-}, S^{2-}, Cl^-	−3 → −1	falls
anions vs cations	—	anions much larger

Cations have lost their outer shell so are smaller than the parent atom; anions have gained electrons, so repulsion expands the shell. Across an isoelectronic series the radius falls as nuclear charge rises.

MARKS LOST HERE

— Saying shielding increases across a period.

— Explaining the Si melting point by London forces rather than a giant covalent network.

— Forgetting that MgO is only sparingly soluble, so its pH is ~9, not 13.

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Chlorides, Hydroxides and Group Trends

13 · CHLORIDES OF PERIOD 3

Chloride	Bonding	With water
NaCl	ionic	dissolves, pH 7
$MgCl_2$	ionic	dissolves, pH ~6.5
Al_2Cl_6	covalent dimer	hydrolyses, pH ~3
$SiCl_4$	simple covalent	hydrolyses fully, pH ~2
PCl_5	simple covalent	hydrolyses fully, pH ~2

Hydrolysis produces **steamy white fumes of HCl**. Ionic chlorides simply dissolve; covalent ones react with water.

14 · HYDROLYSIS EQUATIONS

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$
— the small, highly charged Al^{3+} polarises the water it hydrates, releasing H^+ and giving an acidic solution.

15 · HYDROXIDES

NaOH — strongly basic, very soluble. $Mg(OH)_2$ — sparingly soluble, weakly basic. $Al(OH)_3$ — insoluble and amphoteric: dissolves in both acid and excess NaOH.

$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$ and $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$.

16 · DOWN A GROUP

Property	Trend ↓
atomic radius	increases — more shells
ionisation energy	decreases
electronegativity	decreases
metallic character	increases

Shielding and distance from the nucleus outweigh the rising nuclear charge.

17 · PERIODICITY OF THE ELEMENTS' OXIDATION STATES

Highest oxidation state = group number: Na +1, Mg +2, Al +3, Si +4, P +5, S +6, Cl +7.

Non-metals also form negative states (P −3, S −2, Cl −1). Metals form only positive ones.

18 · OXIDES WITH ACID AND ALKALI

Basic oxides + acid
$MgO + 2HCl \rightarrow MgCl_2 + H_2O$

Acidic oxides + alkali
$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$
$P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$

Amphoteric
Al_2O_3 reacts with both, as in block 09.

19 · SULFUR OXIDES AND ACID RAIN

SO_2 from burning sulfur-containing fuels dissolves to give sulfurous acid, and oxidises in the air to SO_3, which gives sulfuric acid: $SO_3 + H_2O \rightarrow H_2SO_4$.

The result damages limestone buildings, acidifies lakes and leaches nutrients from soil. Flue gases are scrubbed with CaO or $CaCO_3$: $CaO + SO_2 \rightarrow CaSO_3$.

20 · PREDICTING AN UNFAMILIAR ELEMENT

Use position rather than memory. An element in Group 2 of period 4 will have a larger radius and lower first ionisation energy than Ca's neighbours above it, form a 2+ ion, and give a basic oxide and an ionic chloride that simply dissolves.

Always justify with the same three ideas: nuclear charge, shielding and distance.

21 · OBSERVATIONS TO QUOTE

Test	Observation
Na + cold water	melts, floats, fizzes, moves
Mg + steam	bright white flame, white solid
$SiCl_4$ + water	steamy fumes, white precipitate
PCl_5 + water	violent, steamy HCl fumes
NaCl + water	dissolves, no visible change

Describe what is **seen** — fizzing, fumes, a precipitate, a flame colour — not what you infer.

22 · WHY BONDING CHANGES ACROSS THE PERIOD

Δ electronegativity with chlorine falls steadily from Na to P, so the chlorides shift from ionic through polar covalent to simple covalent — and their behaviour with water changes with them.

The same logic explains the oxides. Al sits at the crossover, which is why Al_2O_3 and $AlCl_3$ both show intermediate character.

23 · WORKED EXAMPLE — IDENTIFY THE CHLORIDE

A period-3 chloride is a colourless liquid that fumes in moist air and gives a solution of pH 2 with a white precipitate.

Fumes → covalent, hydrolysed
Liquid at r.t.p. → not PCl_5 (solid)
White precipitate of SiO_2 → **$SiCl_4$**

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

24 · GROUP TRENDS FOR COMPARISON

Group 2 — reactivity increases down the group as ionisation energies fall; hydroxide solubility increases, sulfate solubility decreases.

Group 17 — oxidising power decreases down the group, so a halogen displaces any halide below it. Volatility decreases as London forces grow.

25 · ANSWER STRUCTURE FOR A TREND QUESTION

State the trend, then explain it with all three factors: **nuclear charge**, **shielding** and **distance from the nucleus**, and say which one dominates.

For a structure question the order is: type of structure → type of bonding → strength of the forces broken → the property asked about. Two marks are usually one for each half.

DEFINITIONS TO QUOTE

Amphoteric — reacts with both acids and bases to form a salt and water.

Electronegativity — the ability of an atom to attract a shared pair of electrons in a covalent bond.

First ionisation energy — the energy needed to remove one mole of electrons from one mole of gaseous atoms.

MARKS LOST HERE

— Writing "dissolves" for $SiCl_4$ and PCl_5; they **hydrolyse**, and the observation is steamy HCl fumes.

— Giving pH 7 for $MgCl_2$ solution without noting it is slightly acidic.

— Quoting only one of the two $Al(OH)_3$ equations when asked to prove it is amphoteric.