The Periodic Table: chemical periodicity

Trends across Period 3 in physical properties, the reactions of the elements, oxides and chlorides with oxygen, chlorine and water, acid–base behaviour and pH, and predicting the properties of other elements.

9.1 Periodicity of physical properties of the elements in Period 3

	Na	Mg	Al	Si	P	S	Cl	Ar
Structure	metallic	metallic	metallic	giant molecular	molecular (P_4)	molecular (S_8)	molecular (Cl_2)	atomic

- **Atomic radius** decreases across the period (greater nuclear charge, same shielding). Ionic radii: the positive ions Na^+ to Al^{3+} decrease; the negative ions P^{3-} to Cl^- are larger (an extra shell) and decrease.
- **Melting point** rises from Na to Al (more delocalised electrons and a higher charge on a smaller ion, so stronger metallic bonding), is **highest at silicon** (giant covalent, strong bonds throughout), then is **low** for P, S and Cl (simple molecules with weak id–id forces) and lowest for Ar. S_8 is higher than P_4 and Cl_2 because of its larger molecule and stronger id–id forces.
- **Electrical conductivity** increases from Na to Al (more delocalised electrons), Si is a semiconductor, and the non-metals do not conduct.

Explain a changing structure before describing the trend

The melting-point graph across Period 3 is not one smooth trend because the type of structure changes. Na, Mg and Al are metallic, Si is a giant covalent network, P, S and Cl contain discrete molecules, and Ar consists of individual atoms. Each section of the graph therefore needs a different particle-and-force explanation. Increasing proton number alone cannot explain why silicon's melting point is much higher than phosphorus's.

Worked comparison: silicon melting requires disruption of many strong covalent bonds in its network. Phosphorus melts by overcoming forces between P_4 molecules, without normally breaking the covalent bonds inside them. Sulfur's S_8 molecules have more electrons and greater polarizability than P_4, so their intermolecular attractions are stronger. Do not explain sulfur's higher melting point by claiming the S–S bonds inside its molecules are broken during melting.

The general atomic-radius decrease follows greater nuclear charge across the same principal shell with similar inner-shell shielding. At the change from small cations to larger anions, the ions being compared no longer have the same electron count or occupied shell. Compare Na^+ with Mg^{2+} as an isoelectronic

Note Academy

pair, then compare P^{3-} with S^{2-} separately. Mixing these two series obscures the reason for the radius jump.

> **TRY IT**
>
> Why is silicon not expected to conduct as well as aluminium simply because it has more outer-shell electrons?

Answer: Aluminium has mobile delocalised electrons in a metal. Silicon's valence electrons mainly participate in a covalent network; its semiconductor behaviour differs from metallic conduction. Electron count alone does not establish the availability of mobile carriers.

9.2 Periodicity of chemical properties of the elements in Period 3

Reactions of the elements

- **With oxygen:** $4Na + O_2 \rightarrow 2Na_2O$ (yellow flame), $2Mg + O_2 \rightarrow 2MgO$ (white flame), $4Al + 3O_2 \rightarrow 2Al_2O_3$, $P_4 + 5O_2 \rightarrow P_4O_{10}$, $S + O_2 \rightarrow SO_2$.
- **With chlorine:** $2Na + Cl_2 \rightarrow 2NaCl$, $Mg + Cl_2 \rightarrow MgCl_2$, $2Al + 3Cl_2 \rightarrow Al_2Cl_6$ (written $AlCl_3$), $Si + 2Cl_2 \rightarrow SiCl_4$, $2P + 5Cl_2 \rightarrow 2PCl_5$.
- **With water (Na and Mg only):** $2Na + 2H_2O \rightarrow 2NaOH + H_2$ (vigorous, pH about 14). Mg reacts very slowly with cold water, giving $Mg(OH)_2$ (pH about 9–10), but rapidly with steam to give MgO.

Oxidation numbers

The oxidation number of the element in the oxides (Na_2O +1, MgO +2, Al_2O_3 +3, P_4O_{10} +5, SO_2 +4, SO_3 +6) and the chlorides ($NaCl$ +1, $MgCl_2$ +2, $AlCl_3$ +3, $SiCl_4$ +4, PCl_5 +5) **rises across the period**, equal to the number of outer (valence) electrons used in bonding.

Note Academy

Oxides, structure and reaction with water

Oxide	Bonding	Reaction with water	pH
Na_2O	ionic	$Na_2O + H_2O \rightarrow 2NaOH$	13–14
MgO	ionic	slightly soluble, $MgO + H_2O \rightarrow Mg(OH)_2$	about 9
Al_2O_3	ionic with covalent character	insoluble	7
SiO_2	giant covalent	insoluble	7
P_4O_{10}	covalent	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$	0–2
SO_2	covalent	$SO_2 + H_2O \rightleftharpoons H_2SO_3$	2–3
SO_3	covalent	$SO_3 + H_2O \rightarrow H_2SO_4$	0–1

Acid–base behaviour

- Na_2O and MgO are **basic**: $MgO + 2HCl \rightarrow MgCl_2 + H_2O$. $Mg(OH)_2$ is sparingly soluble, so its saturated solution supplies less OH^- than a readily soluble hydroxide; low solubility should not simply be equated with weak-base ionisation.
- Al_2O_3 and $Al(OH)_3$ are **amphoteric**. They react with acid: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$, and with sodium hydroxide: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$.
- SiO_2 is acidic: it reacts with hot concentrated NaOH, giving Na_2SiO_3.
- P_4O_{10}, SO_2 and SO_3 are **acidic**: $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$.

The trend from basic to acidic follows the change from ionic to covalent bonding as electronegativity of the element rises.

Chlorides with water

- $NaCl$ and $MgCl_2$ (ionic) dissolve with little reaction: pH 7 for NaCl; about 6 for $MgCl_2$ (slight hydrolysis).
- Anhydrous $AlCl_3$ reacts with water. In excess water it forms hydrated aluminium ions, whose hydrolysis makes the solution acidic: $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+$. Do not assume complete precipitation of $Al(OH)_3$ in the resulting acidic solution.
- $SiCl_4$ hydrolyses fully: $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$, pH about 1.
- PCl_5 hydrolyses fully: $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$, pH about 0–1; with a limited amount of water, $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$.

Note Academy

Ionic chlorides conduct when molten; covalent chlorides ($SiCl_4$, PCl_5) are liquids or solids with low melting points and do not conduct. From observations you can suggest the type of bonding in an unknown oxide or chloride.

Acid–base character is established by reactions

A basic oxide reacts with an acid, an acidic oxide reacts with a base, and an amphoteric oxide reacts with both. These definitions concern reactions, not simply whether the solid changes the pH of water. Insoluble SiO_2 does not acidify water appreciably, yet it is an acidic oxide because it reacts with alkali. Insoluble Al_2O_3 is amphoteric rather than neutral.

Worked example: $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ shows basic behaviour towards acid. $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$ shows acidic behaviour towards alkali. Both atoms and charges balance. The hydroxide analogue also dissolves in excess hydroxide, explaining why a precipitate can form and then disappear during a qualitative test.

Numerical pH values depend on the amount added, concentration, temperature and degree of reaction. Treat tabulated ranges as illustrations of relative behaviour, not fixed properties of the solid itself. A suspension that leaves water near neutral has not been proved chemically neutral.

Dissolution, hydrolysis and bonding evidence

NaCl dissolves mainly by separating and hydrating ions already present in its lattice. Silicon tetrachloride reacts with water to form new substances, including HCl. This **hydrolysis** differs from simple dissolution. Moist-air fumes indicate HCl-containing droplets, while the acidic aqueous solution contains hydrogen ions and chloride ions; distinguish observations from explanations.

Worked prediction: an unfamiliar chloride is volatile, does not conduct as a pure liquid and reacts vigorously with water to give an acidic solution. These observations support molecular covalent bonding with hydrolysis, rather than an ionic melt containing freely moving ions. The observation is not enough to identify a unique element without further data.

For phosphorus(V) chloride, the structural description depends on state. Gaseous PCl_5 is molecular; solid PCl_5 has ionic character through $[PCl_4]^+$ and $[PCl_6]^-$. Avoid extending a gas-phase molecular model to every phase without qualification. Aluminium chloride likewise changes association with conditions, so compare like states.

> **TRY IT**
>
> A white oxide is insoluble in water but dissolves in both dilute acid and excess aqueous NaOH. What acid–base description is justified?

Note Academy

Answer: Amphoteric. Water insolubility alone gives no such classification; reactions with both acid and base provide the evidence.

9.3 Chemical periodicity of other elements

The same ideas apply to other periods and groups. Use the **position in the Periodic Table**, electronegativity, bonding type and trends in oxidation number to **predict the properties** of an element or its compounds in a group, or to deduce the **identity and group** of an unknown element from its physical and chemical data (melting point, conductivity, oxide pH, successive ionisation energies).

Combining evidence for an unknown

Worked example: an element has a large jump between its second and third ionisation energies, forms a high-melting oxide and a chloride that conducts when molten. Two removable outer electrons suggest Group 2, and the compound properties support an ionic metal chemistry. An alkaline oxide-water mixture would add supporting evidence. None of these observations alone establishes a particular isotope or exact atomic mass.

When extrapolating, separate a prediction from an observation. State "expected to" and justify the prediction through electron configuration and structure. If provided evidence conflicts with a simple trend, consider a change in structure or bonding rather than forcing the data to fit a memorised graph.

> TRY IT
>
> Why does an acidic aqueous chloride solution not prove that the original chloride contains free hydrogen ions?

Answer: Hydrogen ions can be produced by hydrolysis with water. The chloride may initially contain no hydrogen at all, as in $SiCl_4$. Distinguish starting composition from reaction products.

Chapter check: explain physical properties through structure, classify oxides by reactions, and distinguish dissolution from hydrolysis. Revisit **bonding** where a trend changes abruptly.

References and further reading

Scope follows section 9 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

Note Academy