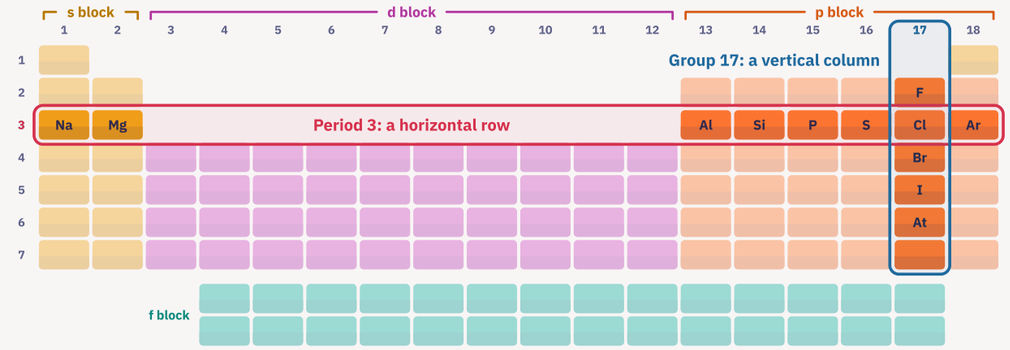
05 The Periodic Table

1 Organisation of the Periodic Table



s block p block d block f block Period 3 Group 17

- **Periodicity**: the _____ of physical and chemical properties at regular intervals, with elements in order of increasing proton number
- Blocks are named after the subshell holding the valence electrons
- **Group** (column): same outer electronic configuration → similar _____ properties. Main group: group number = no. of valence electrons
- **Period** (row): period number = principal quantum number, n, of the _____

2 Atomic and Ionic Radius

2.1 Atomic radius

Atomic radius: half the distance between the nuclei of two adjacent atoms of the same element.

Across Period 3, atomic radius ↓

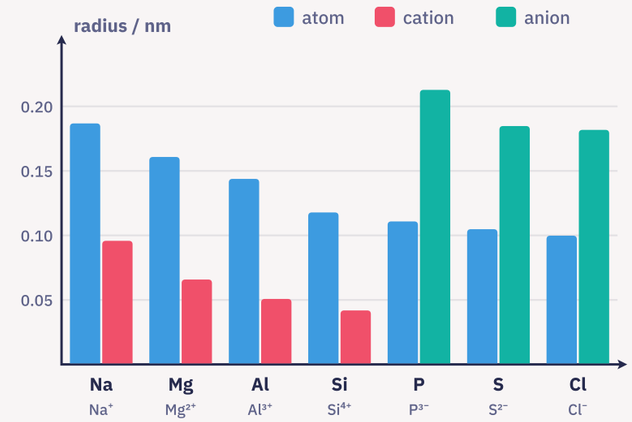
1. Nuclear charge ↑, electrons added to the _____ → shielding approx. constant
2. → stronger attraction between nucleus and valence electrons

Down a group, atomic radius ↑

1. Number of filled _____ _____ ↑
2. → valence electrons further from nucleus and more shielded → weaker attraction

2 Atomic and Ionic Radius (continued)

2.2 Ionic radius



Cation is smaller than its atom

1. Atoms lose some or all of their _____ to form cations
2. → cations usually have _____ principal quantum shell of electrons

Anion is larger than its atom

1. Electrons are added to the outermost principal quantum shell to form anions
2. → greater _____ _____ in the outermost shell

Isoelectronic ions: Na^+ → Si^{4+} and P^{3-} → Cl^-

1. Isoelectronic ions have the _____ _____
2. Atomic number ↑ → nuclear charge ↑ → ionic radius ↓

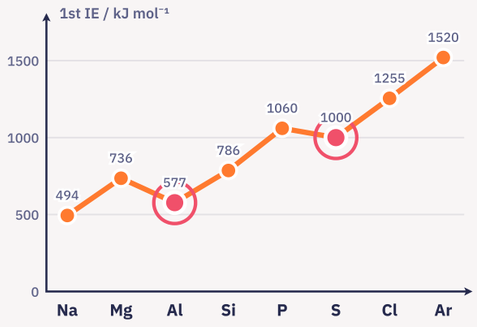
NOTE **P^{3-} ≫ Si^{4+}**: P^{3-} has one _____ filled principal quantum shell.

3 Electronegativity

DEFINITION **Electronegativity**: the ability of an atom to _____ of electrons in a covalent bond.

- **Across** a period ↑: nuclear charge ↑, shielding approx. constant
- **Down** a group ↓: more shells, bonding pair further and more shielded
- Across Period 3, the electronegativity difference with O or Cl ↓ → oxides and chlorides change from _____ to _____

4 First Ionisation Energy



General trend: first IE ↑ across Period 3

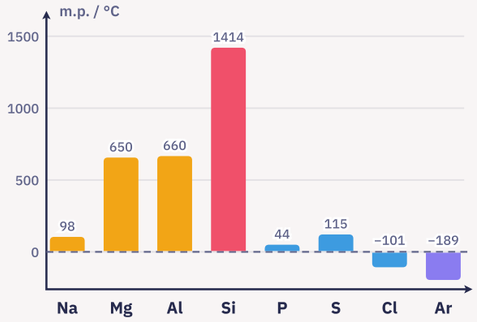
1. Nuclear charge ↑, shielding approx. constant (same shell)
2. → more energy to remove the more strongly attracted valence electron

Down a group: IE ↓ (more shells, more shielding)

Exceptions: the two dips

- **Mg → Al**: 3p e^- removed is higher in energy than 3s
- **P → S**: _____ between the paired 3p e^- in S → one of them is easier to remove than an unpaired 3p e^- from P

5 Melting Point across Period 3



Element	Structure	m.p.
Na, Mg, Al	_____	high, ↑ across
Si	_____	highest
P_4, S_8, Cl_2	_____	low
Ar	monatomic	lowest

Na < Mg < Al

More valence e^- delocalised per atom and smaller, higher-charged cation → stronger _____

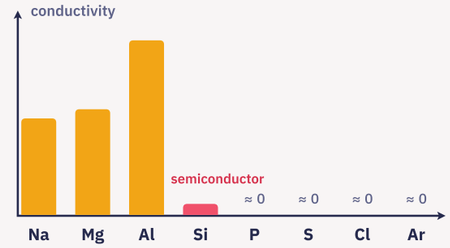
Si

A very large amount of energy is needed to break the extensive network of strong _____

S_8 > P_4 > Cl_2 > Ar

No. of electrons in S_8 > P_4 > Cl_2 > Ar → more energy is needed to overcome the stronger _____ between S_8 molecules than between P_4, then Cl_2 molecules, then Ar atoms

6 Electrical Conductivity across Period 3



1. **Na → Al**: _____ lattice, high conductivity from mobile delocalised electrons
2. Conductivity ↑ Na → Al, as more _____ _____ per atom are delocalised
3. **Si**: sharp drop, giant molecular _____, conducts more as T ↑
4. **P_4 → Ar**: simple molecular or atoms, essentially zero, as there are _____

7 Group 2 Elements

7.1 Reducing power

Reducing power: the ability of an element to lose electrons and reduce another species. Group 2 metals react as $M \rightarrow M^{2+} + 2e^-$.

Why does reducing power ↑ down the group?

1. Down the group, the number of principal quantum shells ↑ → atomic radius ↑
2. Shielding effect ↑, which _____ the increase in nuclear charge
3. → valence e^- _____ by the nucleus → less energy is needed to remove them
4. ∴ M loses its 2 valence e^- more readily → reducing power ↑
5. $E^{\ominus}(M^{2+}/M)$ more negative down the group: Mg −2.38, Ca −2.87, Ba −2.90 V

Examples of differing reducing power: reaction with water

- **Mg**: reacts very slowly with cold water, but readily with steam: $Mg + H_2O(g) \rightarrow MgO + H_2$
- **Ca, Sr, Ba**: react with cold water, increasingly vigorously down the group: $M + 2H_2O \rightarrow M(OH)_2 + H_2$. Solutions become more alkaline

NOTE Group 2 elements only form the +2 state: removing a third e^- means removing an e^- from an inner shell.

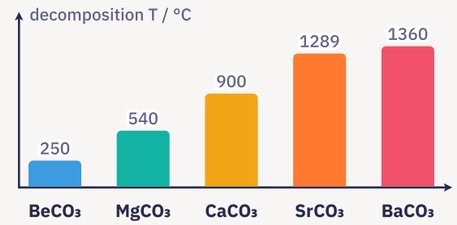
7.2 Thermal stability of carbonates

Thermal stability: the resistance of a compound to decomposition on heating. The thermal stability of Group 2 carbonates _____ down the group.

$$MCO_3(s) \rightarrow MO(s) + CO_2(g)$$

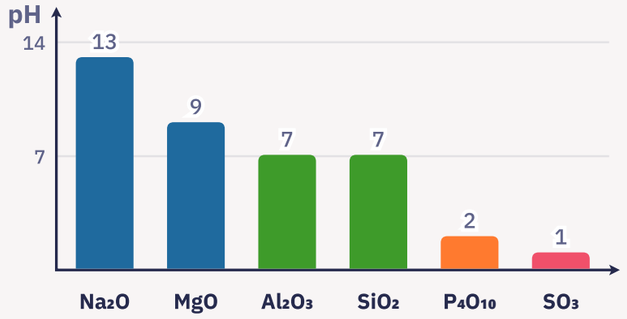
Why does thermal stability ↑ down the group?

1. Down the group, the radius of the metal cation ↑ and its _____ ↓
2. → the ability of M^{2+} to _____ the electron cloud of the large CO_3^{2-} anion ↓, and the C–O bonds are weakened to a smaller extent
3. ∴ more energy is needed to decompose MCO_3 → thermal stability ↑



8 Oxides of Period 3

8.1 Structure, bonding and nature



Oxide	Ox. no.	Structure and bonding	Nature	pH in water
Na_2O	**+1**	giant ionic	_____	**13**
MgO	**+2**	giant ionic	basic	**9**
Al_2O_3	**+3**	giant ionic, _____	_____	**7 (insoluble)**
SiO_2	**+4**	giant molecular	acidic	**7 (insoluble)**
P_4O_{10}	**+5**	simple molecular	acidic	**2**
SO_3	**+6**	simple molecular	acidic	_____

8.2 Equations, in order of the elements

Oxide	With water	With acid	With alkali
Na_2O	$Na_2O + H_2O \rightarrow 2NaOH$	$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$	–
MgO	$MgO + H_2O \rightleftharpoons Mg(OH)_2$	$MgO + 2HCl \rightarrow MgCl_2 + H_2O$	–
Al_2O_3	no reaction	$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$	$Al_2O_3 + 2OH^- + 3H_2O \rightarrow$ _____
SiO_2	no reaction	–	$SiO_2 + 2OH^- \rightarrow$ _____ $+ H_2O$ hot, concentrated NaOH
P_4O_{10}	$P_4O_{10} + 6H_2O \rightarrow$ _____	–	$P_4O_{10} + 12OH^- \rightarrow 4PO_4^{3-} + 6H_2O$
SO_3	$SO_3 + H_2O \rightarrow$ _____	–	$SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O$

EXAM TIP Reactions with water and alkali are not redox: the oxidation number stays the same, so P_4O_{10} (+5) gives H_3PO_4 (+5), not H_3PO_3.

8.3 Why is Al_2O_3 amphoteric?

1. Al^{3+} is small and highly charged → high _____
2. → _____ the electron cloud of O^{2-} → partial covalent character
3. ∴ reacts with both acids and bases

$Al(OH)_3$ is amphoteric too: $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$ and $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$. NaOH and $Mg(OH)_2$ are basic only.

8 Oxides of Period 3 (continued)

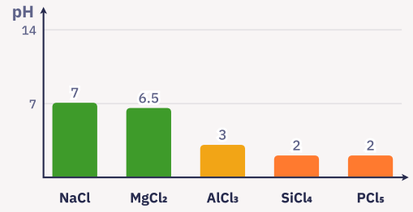
8.4 Why are Al_2O_3 and SiO_2 insoluble?

- **Al_2O_3**: very high _____
- **SiO_2**: extensive network of strong _____
- Not enough energy is released on hydration to overcome these, so pH stays 7

9 Chlorides of Period 3

9.1 Structure and behaviour in water

Chloride	Ox. no.	Structure	With water	pH
NaCl	**+1**	giant ionic	hydration only	**7**
$MgCl_2$	**+2**	giant ionic	hydration, _____ hydrolysis	**6.5**
$AlCl_3$ (Al_2Cl_6)	**+3**	simple molecular	hydration, _____ hydrolysis	**3**
$SiCl_4$	**+4**	simple molecular	_____ hydrolysis	**2**
PCl_5	**+5**	simple molecular	complete hydrolysis	**2**



Highest oxidation number = no. of valence e^-, as every valence e^- is used in bonding to the more electronegative O or Cl: +1 (Na) to +6 (S in SO_3).

9.2 Equations, in order of the elements

Chloride	Excess water	Limited water
NaCl	$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$	–
$MgCl_2$	$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$ $[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H^+$	–
$AlCl_3$	$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$ $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$	$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$ white solid, white fumes
$SiCl_4$	$SiCl_4 + 2H_2O \rightarrow$ _____	–
PCl_5	$PCl_5 + 4H_2O \rightarrow$ _____	$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

9.3 Why is $AlCl_3$(aq) acidic?

1. Al^{3+} has a high _____
2. → strongly _____ the O–H bonds of the water ligands
3. → O–H weakens and breaks, releasing H^+

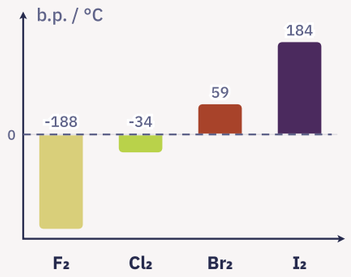
9.4 Why does $SiCl_4$ hydrolyse but not CCl_4?

- **Si** has _____ to accept a lone pair from H_2O
- **C** has no 3d orbitals, and the small C atom is _____ by four large Cl atoms

10 Group 17: The Halogens

10.1 Physical properties

	At r.t.p.	In hexane	In water	X–X / kJ mol⁻¹
F_2	pale yellow gas	very pale yellow	–	**158**
Cl_2	greenish-yellow gas	pale yellow	pale yellow	**244**
Br_2	red-brown liquid	_____	orange	**193**
I_2	black solid	_____	brown	**151**



NOTE F–F is weaker than Cl–Cl: the lone pairs on the two small, close F atoms repel each other.

10.2 Volatility

Volatility: the ease with which a substance changes into a gas. The lower the b.p., the more volatile the substance.

Why does volatility ↓ down the group?

1. All halogens are simple molecular, non-polar X_2 molecules
2. Down the group, M_r ↑ → no. of electrons ↑ → electron cloud more _____ → stronger id–id
3. → _____ is needed to overcome the id–id between X_2 molecules → b.p. ↑ → volatility ↓

10.3 Oxidising power

Oxidising power: the ability of an element to gain electrons and oxidise another species. Halogens react as $X_2 + 2e^- \rightarrow 2X^-$.

Why does oxidising power ↓ down the group?

1. Down the group, the number of principal quantum shells ↑ → atomic radius ↑
2. Shielding effect ↑, which _____ the increase in nuclear charge
3. → the incoming e^- is _____ by the nucleus → X_2 gains electrons less readily
4. ∴ oxidising power ↓: $F_2 > Cl_2 > Br_2 > I_2$
5. $E^{\ominus}(X_2/X^-)$ less positive down the group: F_2 +2.87, Cl_2 +1.36, Br_2 +1.07, I_2 +0.54 V

10.4 Displacement reactions: each halogen with the other halide ions

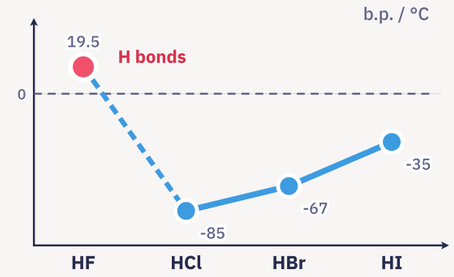
A halogen oxidises the halide ions of the halogens **below** it. Observations are for aqueous solutions, shaking with hexane shows the halogen formed more clearly.

Halogen	Halide	Reaction	Observation
F_2	Cl^-, Br^-, I^-	oxidises all of them	F_2 also oxidises water, so it is not used in aqueous solution
Cl_2	Br^-	$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$	colourless solution turns _____, orange-red in hexane
Cl_2	I^-	$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$	colourless solution turns _____, purple in hexane
Br_2	Cl^-	no reaction	solution stays orange (from Br_2)
Br_2	I^-	$Br_2 + 2I^- \rightarrow 2Br^- + I_2$	orange solution turns _____, purple in hexane
I_2	Cl^-, Br^-	no reaction	solution stays brown (from I_2)

11 Hydrogen Halides

11.1 Boiling points

- **HCl → HI**: more electrons → stronger _____ → b.p. ↑
- **HF**: anomalously high, due to _____



11.2 Thermal stability

HX	H–X / kJ mol⁻¹	On heating
HF	**562**	stable
HCl	**431**	stable
HBr	**366**	some _____ Br_2 fumes
HI	**299**	_____ I_2 fumes with a hot rod

Why does thermal stability decrease down the group?

1. Valence orbital of X is _____ → less effective overlap with H 1s
2. → H–X bond _____ → less energy needed to break it

12 Deducing and Predicting

12.1 Identify element X

X is a solid with very low conductivity at r.t. Its only chloride is a liquid non-conductor, which hydrolyses in water to give a white solid and a strongly acidic solution.

ANSWER STRUCTURE Set out each piece of information beside what you deduce from it, then conclude.

Information	Deduction
solid, very low conductivity	_____
chloride is a liquid non-conductor	_____ chloride
white solid + strongly acidic solution	$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

∴ X is _____

12.2 Predict: astatine, below iodine

Prediction	Reason
less electronegative than I	more shells, more shielding
dark solid, less volatile	more electrons, stronger _____
HAt decomposes more easily	H–At bond _____ than H–I
cannot oxidise Cl^- to Cl_2	weaker _____ than I_2