LEARNERS' ALLEY
Designed by Khow Willard

8 The Periodic Table and Periodicity

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The Periodic Table is more than a list. Its rows and columns repeat patterns in size, energy and reactivity, so the position of an element predicts how it behaves. This chapter explains those patterns from the structure of the atom, follows them across Period 3 and down Groups 1, 2, 17 and 18, and uses them to rank the metals in the reactivity series and to stop iron rusting.

Learning objectives

By the end of this chapter, you can:

Foundation O LEVEL

- describe the trends in Groups 1, 17 and 18
- predict displacement reactions of halogens and of metals
- place metals in the reactivity series from their reactions
- state the conditions for rusting and how it is prevented, including sacrificial protection

Core A LEVEL

- explain the trends in atomic radius, ionic radius, ionisation energy and electronegativity
- explain the melting points and conductivity of the Period 3 elements
- describe the oxides and chlorides of Period 3 and their reactions with water
- explain the trends in Group 2 and Group 17, including thermal stability
- identify an unknown element from its properties

Prerequisites

Chapter 2 (shells, subshells and ionisation energy), Chapter 3 (the Periodic Table, bonding, structure and electronegativity), Chapter 4 (equations), Chapter 5 (acidic, basic and amphoteric oxides) and Chapter 6 (oxidising and reducing agents). Fill in the blanks as the lesson goes.

8.1 Periodicity

Elements are arranged in order of increasing proton number. As you go along, properties repeat at regular intervals. This repeating pattern is **periodicity**.

Periodicity is the _____ of chemical and physical properties seen at regular intervals in the Periodic Table.

Chapter 3 showed that the group gives the number of valence electrons and the period gives the number of shells. Two more facts complete the picture:

- The table divides into blocks named after the subshell being filled (Chapter 2): Groups 1 and 2 are the **s-block**, Groups 13 to 18 the **p-block** and Groups 3 to 12 the **d-block**.
- Elements in a group have the same outer electron configuration, so they have _____.

Across a period the elements change from metals to non-metals, and their oxides change from basic through amphoteric to acidic (Chapter 5). Down a group, metallic character increases. Figure 8.1 sums up the trends that the next section explains.

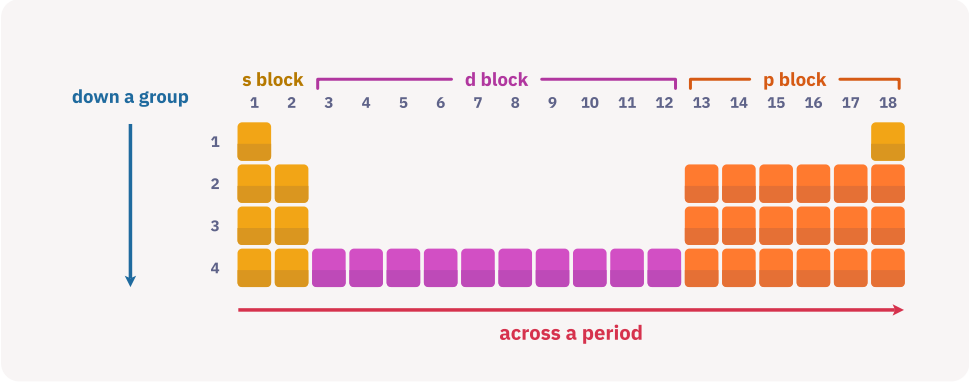


Figure 8.1 The blocks of the Periodic Table, and the two directions the trends run: across a period and down a group.

Check your understanding

1. Why do sodium and potassium have similar chemical properties?

8.2 Trends in atomic properties

CORE · A LEVEL

Every trend in this section comes from three things you met in Chapter 2: the **nuclear charge**, the number of **shells**, and **shielding** by inner electrons.

- **Across a period**, the nuclear charge increases, but the electrons go into the same outer shell, so shielding stays about the same. The outer electrons are pulled in _____.
- **Down a group**, each element has one more filled shell. The outer electrons are further from the nucleus and more shielded, so they are held _____, even though the nuclear charge is larger.

8.2.1 Atomic and ionic radius

The **atomic radius** is half the distance between the nuclei of two neighbouring atoms of the element. It **decreases** across a period and **increases** down a group (Figure 8.2).

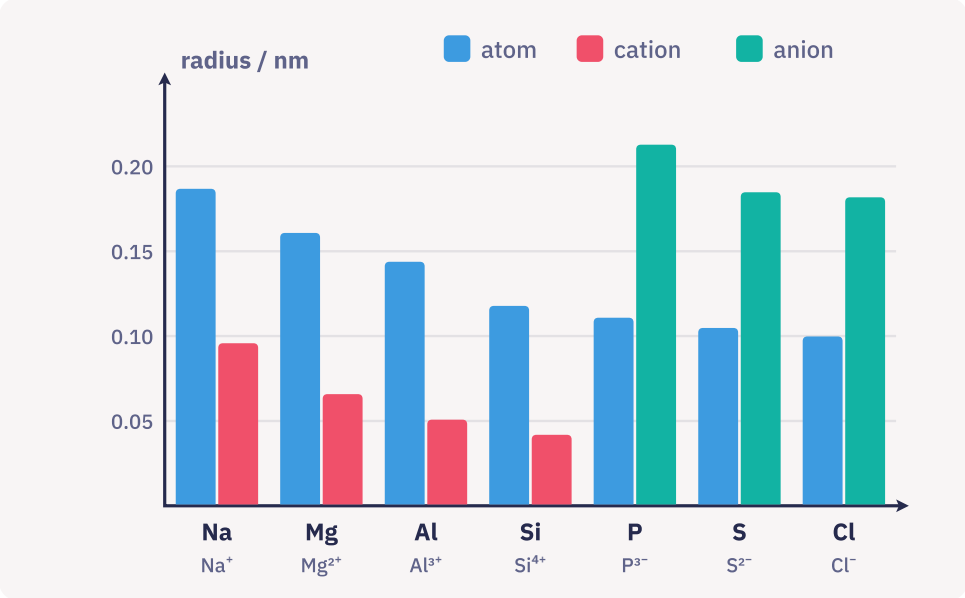


Figure 8.2 Atomic and ionic radii across Period 3, in nm (data from the A Level Data Booklet).

- A **cation** is smaller than its atom: it has lost its outer shell, and the same nuclear charge pulls on fewer electrons.
- An **anion** is larger than its atom: the extra electrons repel one another and spread out.
- Na^+ to Si^{4+} are **isoelectronic** (Chapter 2), so the radius falls as the nuclear charge rises. The same is true of P^{3-} to Cl^-. P^{3-} is much larger than Si^{4+} because it has one more shell.

8.2.2 First ionisation energy

The **first ionisation energy** is the energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms, to form 1 mole of singly charged gaseous cations (Chapter 2). For sodium, $Na(g) \rightarrow Na^+(g) + e^-$.

- **Across a period** it generally **increases**. The nuclear charge rises, but the electrons enter the same shell, so the shielding stays about the same. The outer electron is held more strongly, so more energy is needed to remove it.
- **Down a group** it **decreases**. The outer electron is in a shell further from the nucleus and more shielded by the inner shells. It is held less strongly, even though the nuclear charge is larger.

Period 3 has two dips in this rise (Chapter 2 drew the graph):

1 Al (577 kJ mol^{-1}) is lower than Mg (736 kJ mol^{-1})

Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ Al: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

- The electron removed from Al is in the 3p subshell, which is _____ than the 3s, so it is easier to remove.

2 S (1000 kJ mol^{-1}) is lower than P (1060 kJ mol^{-1})

P: ...$3s^2\ 3p^3$ S: ...$3s^2\ 3p^4$

- The electron removed from S is _____ in a 3p orbital. Repulsion between the two electrons in that orbital makes it easier to remove.

EXAM TIP Do not swap the two reasons. The Mg/Al dip is about a **higher-energy subshell** (3p above 3s). The P/S dip is about **pairing** in one orbital.

8.2.3 Electronegativity

In Chapter 3 we met electronegativity briefly, as a rough picture: metals have few valence electrons and attract a shared pair weakly, while non-metals are close to a full shell and attract it strongly. Here we look at what electronegativity really is, how it varies and why.

DEFINITION **Electronegativity** is the ability of an atom in a covalent bond to attract the _____ of electrons towards itself.

The shared pair is pulled by the nucleus of each bonded atom, through that atom's inner electrons. So electronegativity depends on the same things as ionisation energy: the nuclear charge, the distance of the shared pair from the nucleus, and the shielding.

- **Across a period** it **increases**. The nuclear charge rises with about the same shielding, and the atom gets smaller, so the shared pair is closer to the nucleus. Both pull the shared pair more strongly.
- **Down a group** it **decreases**. Each element has one more filled shell, so the shared pair is further from the nucleus and more shielded. This outweighs the larger nuclear charge.

Fluorine, top right, is the most electronegative element.

GOING FURTHER Because electronegativity rises across but falls down, an element can resemble the one diagonally below and to its right: lithium and magnesium, beryllium and aluminium, boron and silicon. Like aluminium hydroxide, beryllium hydroxide is amphoteric.

Check your understanding

1. Explain why the radius of Mg^{2+} (0.065 nm) is much smaller than that of a Mg atom (0.160 nm).
2. Explain why the first ionisation energy of sulfur is lower than that of phosphorus.

8.3 The Period 3 elements

CORE · A LEVEL

The melting point and conductivity of each Period 3 element follow from its structure (Chapter 3 and Figure 8.3).

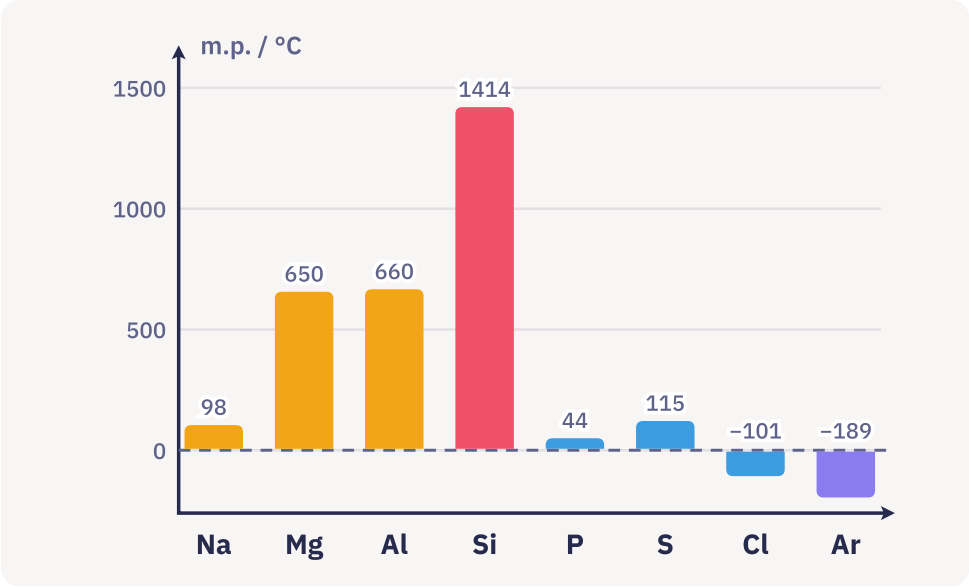


Figure 8.3 Melting points across Period 3, in °C: rising through the giant metallic elements to giant covalent silicon, then low for the simple molecular elements and argon.

element	Na	Mg	Al	Si	P	S	Cl
melting point / °C	98	650	660	1414	low	115	−101
structure	giant metallic			giant covalent	simple molecular: P_4, S_8, Cl_2		

- **Na, Mg, Al**: the number of delocalised electrons per atom rises (1, 2, 3) and the cation gets smaller and more highly charged, so metallic bonding gets stronger (Chapter 3). Melting point and conductivity rise.
- **Si**: a giant covalent structure. Very many strong covalent bonds must break, so it has the _____ melting point. It is a **semiconductor**: it conducts a little, more at higher temperature.
- **P, S, Cl**: simple molecules held by weak instantaneous dipole–induced dipole forces, so low melting points. S_8 > P_4 > Cl_2, the order of the number of electrons in each molecule. They do not conduct: no mobile electrons or ions.

Check your understanding

1. Why does aluminium conduct electricity better than sodium?
2. Why is the melting point of sulfur higher than that of chlorine?

8.4 Oxides and chlorides of Period 3

CORE · A LEVEL

In its highest oxide or chloride, each element's oxidation state equals its number of valence electrons: +1 in Na_2O up to +6 in SO_3, and +1 in NaCl up to +5 in PCl_5. It is always positive, because oxygen and chlorine are more electronegative than every Period 3 element.

Across the period the electronegativity difference between the element and oxygen or chlorine **shrinks**, so the bonding changes from **ionic** to **covalent**. Structure decides behaviour: ionic oxides are basic, covalent oxides are acidic (Figure 8.4).

8.4.1 The oxides

oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3
structure	giant ionic		giant ionic, some covalent character	giant covalent	simple molecular	
nature	basic		_____	acidic		
pH in water	13	9	7 (insoluble)	7 (insoluble)	2 to 3	1

1 Basic oxides: Na_2O and MgO

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq) \quad \text{strongly alkaline}$$

$$MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq) \quad \text{sparingly soluble, weakly alkaline}$$

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

2 Amphoteric: Al_2O_3

Insoluble in water, but reacts with acids and with sodium hydroxide:

$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq), \text{ sodium aluminate}$$

3 Acidic oxides: SiO_2, P_4O_{10}, SO_3

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq) \qquad SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

$$SiO_2(s) + 2NaOH(conc) \rightarrow Na_2SiO_3(aq) + H_2O(l) \quad \text{only with hot concentrated alkali}$$

- SiO_2 is insoluble in water: too many strong covalent bonds would have to break.
- These reactions are not redox: P stays +5 in H_3PO_4 and S stays +6 in H_2SO_4.

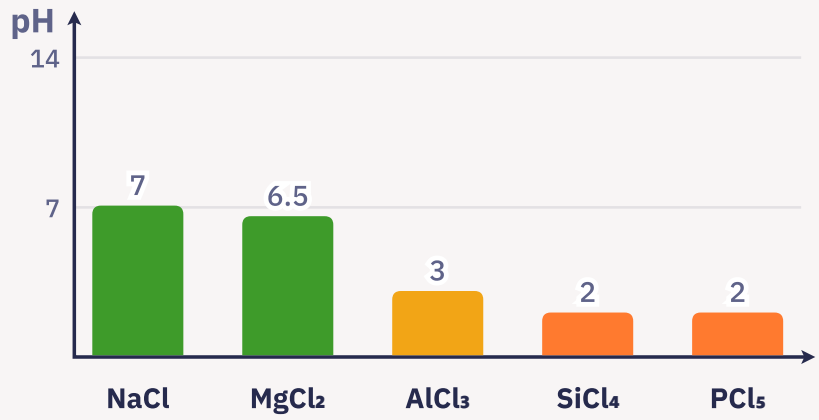


Figure 8.4 pH of the solutions formed by the Period 3 chlorides in water. The oxides are in the table above.

8.4.2 The chlorides

chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
structure	giant ionic		simple molecular ($AlCl_3$ forms Al_2Cl_6 in the vapour)		
with water	dissolves	dissolves, slight hydrolysis	dissolves, hydrolyses	hydrolyses completely	
pH	7	6.5	3	2	2

Hydrolysis is the breaking of bonds by water. A small, highly charged cation such as Al^{3+} pulls electron density from the water molecules around it so strongly that they release H^+:

$$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$$

Na^+ is too large and weakly charged to do this, so NaCl gives a neutral solution. The covalent chlorides react completely with water, giving white fumes of HCl:

$$SiCl_4(l) + 4H_2O(l) \rightarrow SiO_2{\cdot}2H_2O(s) + 4HCl(aq) \qquad PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$

Check your understanding

1. Explain why Na_2O gives an alkaline solution but SO_3 gives an acidic one.
2. Element X is a solid of low conductivity. Its only chloride is a liquid that does not conduct and reacts with water to give a white solid and a strongly acidic solution. Identify X.

8.5 Group 1: the alkali metals

Lithium, sodium, potassium, rubidium and caesium each have **one** valence electron, which they lose to form M^+ ions.

- They are **soft** (they can be cut with a knife), have **low densities** (lithium, sodium and potassium float on water) and low melting points.
- Their freshly cut surface is shiny but tarnishes quickly, so they are stored in oil.
- Melting points **decrease** down the group: Li 180 °C, Na 98 °C, K 63 °C, Rb 39 °C, Cs 29 °C. The metallic bond weakens as the atoms get larger.

1 alkali metal + water → metal hydroxide + hydrogen

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

- Lithium reacts quickly and floats. Sodium darts around and may explode. Potassium reacts very violently.
- The solution is an alkali, which gives the group its name.

Reactivity _____ down the group. The atom gets larger, so its single valence electron is further from the nucleus and more shielded, and is lost more easily. Each metal is a reducing agent (Chapter 6), and the reducing power increases down the group.

Check your understanding

1. Write the equation for rubidium reacting with water, and name the products.

8.6 Group 2

CORE · A LEVEL

Uses of Group 2 compounds: MgO lines furnaces (high melting point, low reactivity), $CaCO_3$ (limestone) is a building material, CaO (quicklime) treats acidic soil, and $BaSO_4$ is the barium meal in X-ray diagnosis.

Magnesium to barium have two valence electrons and form only M^{2+} ions: removing a third electron would mean breaking into an inner shell. Like Group 1, they become more reactive down the group, as the two outer electrons are lost more easily: their reducing power increases.

metal	with water
Mg	very slowly with cold water, quickly with steam: $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$
Ca	readily with cold water: $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2 + H_2(g)$
Sr, Ba	with cold water, increasingly vigorously, giving more strongly alkaline solutions

8.6.1 Thermal stability of the carbonates

Group 2 carbonates break down on heating: $MCO_3(s) \rightarrow MO(s) + CO_2(g)$. The temperature needed rises down the group (Figure 8.5), so the carbonates become more _____.

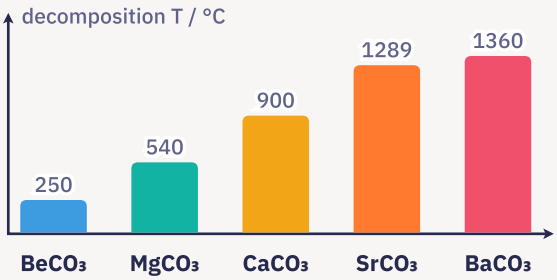


Figure 8.5 Temperatures at which the Group 2 carbonates decompose.

Why: down the group the M^{2+} ion gets larger, so its **charge density** (charge ÷ size) falls. A small, highly charged ion such as Mg^{2+} pulls on the electron cloud of the large carbonate ion and distorts it (**polarises** it), weakening the C–O bonds inside it. The carbonate then breaks up more easily. Ba^{2+} distorts it least, so $BaCO_3$ is the most stable.

Check your understanding

1. Which decomposes at a lower temperature, calcium carbonate or barium carbonate? Explain.

8.7 Group 17: the halogens

Uses of the halogens: fluoride goes in toothpaste, chlorine disinfects water and ClO^- is the active part of bleach, silver bromide is in photographic film, and tincture of iodine is an antiseptic.

The halogens are non-metals made of diatomic molecules. Each atom has seven valence electrons and gains one to form a halide ion, X^-.

halogen	state and colour at room temperature	melting point / °C
chlorine, Cl_2	**yellow-green gas**	**−101**
bromine, Br_2	**red-brown liquid**	**−7**
iodine, I_2	**purple-black solid**	**114**

Down the group the colours get **darker** and the melting and boiling points **increase**. The molecules have more electrons, so the instantaneous dipole–induced dipole forces between them are stronger. The halogens become **less volatile**.

8.7.1 Reactivity and displacement

A halogen reacts by gaining an electron, so it is an **oxidising agent**. Reactivity _____ down the group: the larger the atom, the further the incoming electron is from the nucleus and the more it is shielded, so it is attracted less strongly.

1 A more reactive halogen displaces a less reactive one from its halide

$$Cl_2(aq) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(aq) \quad \text{colourless to red-brown}$$

$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$ $Br_2(aq) + 2KI(aq) \rightarrow 2KBr(aq) + I_2(aq)$ colourless to brown

- A less reactive halogen cannot displace a more reactive one: Br_2 does not react with KCl, and I_2 reacts with neither KCl nor KBr.
- Each displacement is a redox reaction: the halogen is reduced and the halide ion is oxidised.

WORKED EXAMPLE Astatine is below iodine in Group 17. Predict what happens when chlorine is bubbled into sodium astatide solution.

1. Chlorine is above astatine, so it is more reactive. *Reactivity decreases down the group.*

2. _____: chlorine displaces astatine. *Chlorine is reduced, astatide ions are oxidised.*

8.7.2 Hydrogen halides CORE · A LEVEL

The hydrogen halides become less stable to heat down the group. HF does not decompose even on strong heating, but HI gives purple fumes of iodine with a hot rod: $2HI(g) \rightarrow H_2(g) + I_2(g)$. The larger halogen atom overlaps less well with hydrogen, so the bond gets weaker:

bond	H–F	H–Cl	H–Br	H–I
bond energy / kJ mol^{-1}	562	431	366	299

GOING FURTHER The falling oxidising power shows in their reactions with thiosulfate. Chlorine and bromine oxidise $S_2O_3^{2-}$ all the way to SO_4^{2-} (S from +2 to +6), but iodine takes it only to $S_4O_6^{2-}$ (to +2.5), the reaction used in iodine titrations (Chapter 6).

Check your understanding

1. Describe and explain what you see when bromine water is added to potassium iodide solution.

2. Why is HI less thermally stable than HCl?

8.8 Group 18: the noble gases

Helium, neon, argon, krypton, xenon and radon are colourless, monatomic gases with low melting and boiling points. Helium has two valence electrons and the others eight: their outer shells are _____, so they rarely lose, gain or share electrons. They are very unreactive and are used where an **inert atmosphere** is needed: argon in steel-making and light bulbs, helium in balloons, neon in coloured lamps.

Check your understanding

1. Why are the noble gases unreactive?

8.9 The reactivity series

Metals can be placed in order of reactivity from how they react with water, steam and dilute acid (Figure 8.6). A more reactive metal loses its electrons more readily to form positive ions. Carbon and hydrogen are included, because they can reduce some metal oxides.

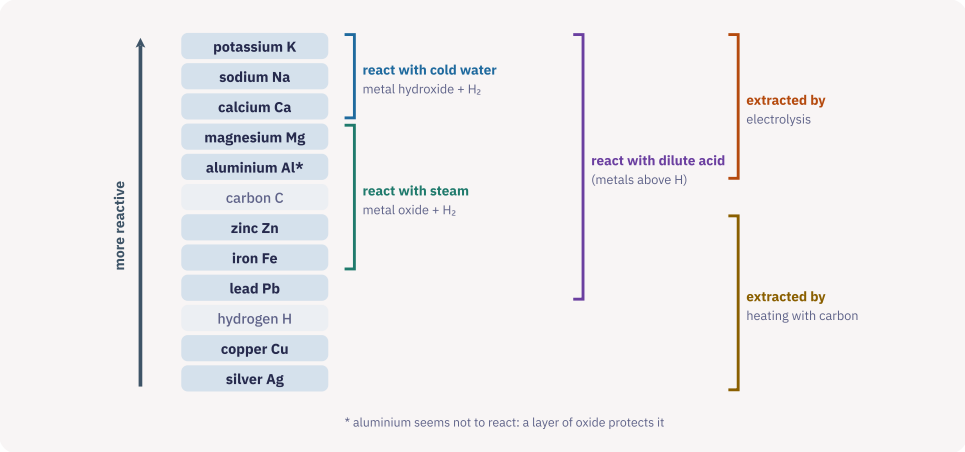


Figure 8.6 The reactivity series, with the reactions and extraction methods that follow from it.

- Metals above hydrogen react with dilute hydrochloric acid to give hydrogen. Lead seems not to, because insoluble lead(II) chloride coats it (Chapter 5).
- Aluminium seems unreactive because a thin layer of aluminium oxide protects it.

1 A more reactive metal displaces a less reactive metal from its compounds

from a solution: $Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ $\quad Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

from an oxide: $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$

- The more reactive metal is oxidised and the less reactive metal ion is reduced: a redox reaction (Chapter 6).

2 Carbon or hydrogen reduces the oxides of metals below it

$2CuO(s) + C(s) \rightarrow 2Cu(s) + CO_2(g)$ $\quad PbO(s) + H_2(g) \rightarrow Pb(s) + H_2O(g)$

- This is how metals below carbon, such as zinc, iron and lead, are extracted from their ores. Metals above carbon are extracted by electrolysis (Chapter 13).

3 The more reactive the metal, the more stable its carbonate to heat

- Sodium and potassium carbonates do not decompose. Calcium to copper carbonates break down to the oxide and carbon dioxide. Silver carbonate goes all the way to silver.

WORKED EXAMPLE Chromium does not react with zinc sulfate solution, but a heated mixture of chromium and iron(III) oxide reacts. Where does chromium go in the reactivity series?

1. Cr cannot displace zinc, so Cr is below Zn. — *A less reactive metal cannot displace a more reactive one.*

2. Cr displaces iron from its oxide, so Cr is above Fe: _____. — *Cr is oxidised, Fe^{3+} is reduced.*

Check your understanding

1. Excess zinc powder is added to blue copper(II) sulfate solution. Describe what you see and write the ionic equation.

2. Tin is between iron and lead. Suggest how tin is extracted from tin(II) oxide.

8.10 Corrosion and its prevention

Rusting is the corrosion of iron: its slow oxidation to hydrated iron(III) oxide.

$$4Fe(s) + 3O_2(g) + 2xH_2O(l) \rightarrow 2Fe_2O_3 \cdot xH_2O(s)$$

Rusting needs both _____ (Figure 8.7). Salt speeds it up, and so do acidic gases such as sulfur dioxide, so iron near the sea or in industrial areas rusts faster. Rust is flaky and falls off, exposing fresh iron, so rusting carries on until the metal is gone.

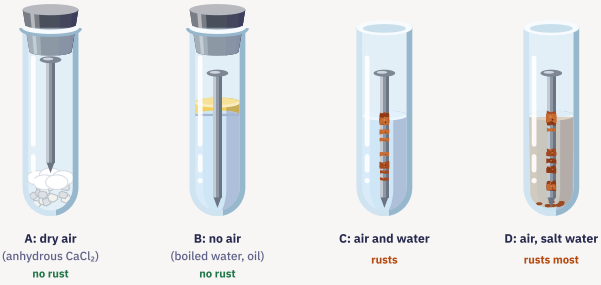


Figure 8.7 Iron nails after one week under different conditions.

1 Barrier methods: keep out oxygen and water

- Painting (cars, ships, bridges), oiling or greasing (machine parts), coating with plastic (kitchenware), tin-plating (food cans), chrome-plating (taps).
- If the barrier is scratched, the iron underneath rusts.

2 Sacrificial protection: a more reactive metal corrodes instead

- Zinc or magnesium is more reactive than iron, so it loses electrons in preference: $Zn \rightarrow Zn^{2+} + 2e^-$ instead of $Fe \rightarrow Fe^{3+} + 3e^-$.
- **Galvanising** coats iron with zinc. It protects even when scratched, because the zinc still corrodes first.
- Blocks of zinc or magnesium are bolted to ships' hulls and underground pipes, and replaced as they corrode.

EXAM TIP Tin-plating is a barrier only. Tin is **less** reactive than iron, so once the coating is scratched the iron rusts. Zinc is more reactive, so galvanised iron is still protected.

Check your understanding

1. Why does a scratched galvanised bucket not rust, while a scratched tin can does?
2. Suggest how rusting is prevented on the parts of a steel pier under water.

Answers to Check your understanding

8.1

1. Both are in Group 1 and have one valence electron, so they react in the same way.

8.2

1. Mg^{2+} has lost its outer (third) shell, and the same nuclear charge (12+) pulls on 10 electrons instead of 12.
2. The electron removed from S is paired in a 3p orbital. Repulsion between the paired electrons makes it easier to remove than the unpaired 3p electron of P.

8.3

1. Each aluminium atom gives three delocalised electrons and each sodium atom only one, so there are more mobile charge carriers.
2. S_8 molecules have more electrons than Cl_2 molecules, so the instantaneous dipole–induced dipole forces between them are stronger.

8.4

1. Na_2O is ionic: $Na_2O + H_2O \rightarrow 2NaOH$. SO_3 is covalent: $SO_3 + H_2O \rightarrow H_2SO_4$.
2. Silicon. Its chloride $SiCl_4$ is a simple molecular liquid that hydrolyses: $SiCl_4 + 4H_2O \rightarrow SiO_2{\cdot}2H_2O + 4HCl$.

8.5

1. $2Rb + 2H_2O \rightarrow 2RbOH + H_2$: rubidium hydroxide and hydrogen.

8.6

1. Calcium carbonate. Ca^{2+} is smaller than Ba^{2+}, so it has a higher charge density and polarises the carbonate ion more, weakening its C–O bonds.

8.7

1. The colourless solution turns brown: bromine is more reactive and displaces iodine. $Br_2 + 2KI \rightarrow 2KBr + I_2$.
2. The H–I bond (299 kJ mol^{-1}) is weaker than H–Cl (431 kJ mol^{-1}).

8.8

1. Their outer shells are full, so they do not need to lose, gain or share electrons.

8.9

1. Red-brown copper forms and the blue colour fades: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.
2. Heat tin(II) oxide with carbon: $2SnO + C \rightarrow 2Sn + CO_2$.

8.10

1. Zinc is more reactive than iron, so it corrodes instead of the iron even where the coating is scratched. Tin is less reactive than iron, so it only works as a barrier.
2. Attach blocks of a more reactive metal, such as zinc or magnesium (sacrificial protection).