CAIE Chemistry A-level

9: The Periodic Table

Notes

Periodicity of Physical Properties of the Elements in Period 3

Atomic Radius

The atomic radius is measured by the distance between the outermost electron and the nucleus, this is done by measuring the distance between the nuclei of two atoms of the same element and halving this.

When comparing the atomic radius of period 3 atoms, the term **metallic radii** is used for metals and **covalent radii** is used for non-metals.

Across period 3, **atomic radius decreases from sodium to chlorine**. The radius of argon can't be compared as its atoms do not bond covalently with each other, so they do not have covalent radii to be compared. Across the period, the atomic number increases, so the **nucleus has a higher positive charge**. This increases the attraction between the nucleus and the outermost electrons, pulling them closer to the nucleus. This decreases the atomic radius. The shielding effect stays the same.

Ionic Radius

The ionic radius is the distance between the nucleus and the outermost electrons in an ion. Across period 3, the ionic radius **decreases from sodium to aluminium** (positively charged ions) and **increases from silicon to chlorine** (negatively charged ions).

The **cations** (positively charged ions) have a **decreasing ionic radius** because they lose electrons to form cations, but the number of protons in the nucleus are increasing. So the positive **nuclear attraction increases**, pulling the outer electrons closer.

The **anions** (negatively charged ions) have an **increasing ionic radius** because the ions gain electrons so there are more electrons than protons. As a result, the nuclear attraction to the electrons is weaker so they are not pulled in as strongly.

Melting Point

The melting points of elements in period 3 depend on their structure and bondingL

- **Sodium**, **magnesium** and **aluminium** are **giant metallic structures** with **metallic bonding**, Their melting points **increases** across the period as the number of delocalized electrons per atom increase to form the metallic ions, so the nuclear attraction increases. This results in stronger metallic bonds which require more energy to overcome and so a higher melting point.
- **Silicon** has a **giant covalent structure**, so requires a lot of energy to overcome the many strong **covalent bonds**, so has a high melting point.
- **Phosphorus** (P_4), **sulfur** (S_8) and **chlorine** (Cl_2) are all **simple covalent** molecules. Their melting points are dependent on the strength of their **van der Waals**/intermolecular forces. The more electrons there are, the stronger the van der Waals forces, so sulfur has the greatest melting point of these three molecules. Chlorine has the lowest melting point of these three since it has fewer electrons so weakest forces to overcome.
- **Argon** will have the **lowest melting point** of period 3 as it exists as single atoms, so there are very weak van der Waals forces that don't require a lot of energy to overcome.

Electrical Conductivity

The conductivity of a compound relies on the presence of **charged particles** (such as ions or electrons) which are free to move.
Metallic compounds can conduct electricity due to the sea of **delocalised electrons.**
Conductivity **increases from sodium to aluminium** because the number of delocalised electrons increases so more electrons are **free to carry charge**.
The molecules silicon to chlorine are **covalent compounds with no charged particles** so they are non-conductors. Similarly argon is monatomic so is unable to conduct electricity.

First Ionisation Energy

The first ionisation energy is the energy required to **remove one mole of electrons** from **one mole of gaseous atoms** to **form one mole of gaseous ions.**

First ionisation energy **generally increases** across period 3. This is because the number of protons increases across the period, **increasing the positive nuclear charge** while electron shielding remains the same. As a result, across the period, the **electrons are attracted more strongly** to the nucleus so they are harder to remove, leading to a higher first ionisation energy.

Exceptions to the trend:

- The first ionisation energy of **aluminium** is **lower** than that of magnesium. This is because the outermost electron of aluminium is in a **3p orbital** rather than a 3s orbital, which is higher energy than the s sub-level, and experiences more shielding from the 3s orbital. Therefore less energy is required to remove this electron
- The first ionisation energy of **sulfur** is **lower** than that of phosphorus. Sulfur is the first element to have an electron pair in a 3p orbital so an electron is being removed from a pair. The electrons in the pair repel each other slightly making it easier to remove an electron.

Periodicity of Chemical Properties of the Elements in Period 3

Reactions with Oxygen

- **Sodium** burns in oxygen with an **orange flame** to produce a **white solid.**

$$4Na + O_2 \rightarrow 2Na_2O$$

- **Magnesium** burns in oxygen with a **bright white flame** to produce a **white solid.**

$$2Mg + O_2 \rightarrow 2MgO$$

- **Aluminium** burns in oxygen if the **aluminium oxide layer** on the outside of the metal is removed, done by **powdering** the aluminium. **Sparks** can be seen when the powder is burned. Aluminium burns in oxygen with a **bright white flame** and a **white solid** is produced.

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

- **Silicon** will only burn in oxygen if it is heated strongly enough.

$$Si + O_2 \rightarrow SiO_2$$

- **White phosphorus** reacts **spontaneously** in the air to produce a **white solid.**

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

- **Sulfur** burns with a **blue flame** in oxygen when heated gently. It produces a colourless gas of **sulfur dioxide** which reacts further with oxygen to form **sulfur trioxide.**

$$S + O_2 \rightarrow SO_2$$
$$2SO_2 + O_2 \rightarrow 2SO_3$$

- **Chlorine** does not react with oxygen (directly).
- **Argon** does not react with oxygen.

Reactions with Chlorine

- **Sodium** burns in chlorine with a **bright orange flame** to form sodium chloride (white solid).

$$2Na + Cl_2 \rightarrow 2NaCl$$

- **Magnesium** burns in chlorine with a **bright white flame** to form magnesium chloride (white solid).

$$Mg + Cl_2 \rightarrow MgCl_2$$

- **Aluminium** burns in a stream of chlorine to produce **pale yellow aluminium chloride.**

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

- If **chlorine** is passed over silicon powder, a **colourless liquid** forms (silicon tetrachloride).

$$Si + 2Cl_2 \rightarrow SiCl_4$$

- **White phosphorus** burns **spontaneously** in chlorine to produce phosphorus(V) chloride (off-white solid), with **excess chlorine**.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

Reactions with Water

- **Sodium** undergoes a very **exothermic** reaction with cold water, producing hydrogen (seen as bubbles) and a colourless solution of sodium hydroxide.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

- **Magnesium** reacts **slowly** with **cold water.** Bubbles of hydrogen are produced and a thin layer of magnesium hydroxide forms on the magnesium which inhibits further reaction.

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

  Magnesium burns in **steam** with a **bright white flame** to produce white magnesium oxide and hydrogen:

$$Mg + H_2O\ (g) \rightarrow MgO + H_2$$

Variation in Oxidation Numbers

Oxidation states can be worked out using the following rules:

- The oxidation state of an uncombined element is 0.
- The sum of oxidation states in a compound is 0 and the sum of oxidation states in an ion is equal to the overall charge.
- Common oxidation states:
  - +1 for group one atoms
  - +2 for group two atoms
  - -2 for oxygen (except when in a peroxide or F_2O)
  - +1 for hydrogen (except in metal hydrides where it is -1)
  - -1 for fluorine
  - -1 for chlorine (except when bonded with fluorine or oxygen)

The oxidation states of Group 3 oxides are shown in the table below:

Compound	**Oxidation state of non-oxygen element**
Na_2O	+1
MgO	+2
Al_2O_3	+3
SiO_2	+4
P_4O_{10}	+5
SO_2	+4
SO_3	+6

The oxidation states of Group 3 chlorides are shown in the table below:

Compound	Oxidation state of non-chlorine element
NaCl	+1
$MgCl_2$	+2
$AlCl_3$	+3
$SiCl_4$	+4
PCl_5	+5

In each of the cases above, the oxidation state has the same value as the number of **valence shell electrons** (the number of electrons in the outer energy level of the atom).

Period 3 Oxides and Water

- **Sodium oxide** is a strongly basic oxide which reacts **exothermically** with water to form a solution of sodium hydroxide (**around pH 14**).

$$Na_2O + H_2O \rightarrow 2NaOH$$

- **Magnesium oxide** undergoes a slight reaction with water, forming some **magnesium hydroxide** ions. As these are only **partially soluble**, the pH of the resulting solution is about 9 since not many hydroxide ions are released into the solution.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

- **Aluminium oxide** does not react with water at room temperature.
- **Silicon dioxide** does not react with water because it is difficult to break up the giant covalent structure
- **Phosphorus(V) oxide** reacts **violently** with water to form **phosphoric acid**

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

- **Sulfur dioxide** reacts with water to form an acidic solution of **sulfurous acid.**

$$SO_2 + H_2O \rightarrow H_2SO_3$$

- **Sulfur trioxide** reacts **violently** with water to produce **sulfuric acid.**

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Acid/Base Behaviour of Period 3 Oxides and Hydroxides

Oxides:

- **Sodium oxide** is a **strong base** which reacts with acid to form a salt and water.

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

- **Magnesium oxide** is a **base** which reacts with warm dilute hydrochloric acid to form a salt and water.

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

- **Aluminium oxide** is **amphoteric** so reacts with **acids and bases**. It reacts with hot dilute hydrochloric in the same way as magnesium and sodium:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

Aluminium oxide also reacts with bases, such as hot, concentrated sodium hydroxide solution:

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

- **Silicon dioxide** is **very weakly acidic** and reacts with hot concentrated sodium hydroxide solution. A **colourless solution** is formed.

$$SiO_2 + NaOH \rightarrow Na_2SiO_3 + H_2O$$

- **Phosphorus(V) oxide** is **very weakly acidic** and can form a **range of salts** when reacted with a base. Here is one example:

$$P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$$

- **Sulfur dioxide** will react with a base, such as sodium hydroxide solution, when bubbled through it, first producing sodium sulfite solution.

$$SO_2 + NaOH \rightarrow Na_2SO_3 + H_2O$$

- **Sulfur trioxide** when reacted with water forms sulfuric acid droplets, a strong acid. Sulfuric acid reacts with sodium hydroxide to form sodium sulfate solution.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O$$

Hydroxides:

- **Sodium and magnesium hydroxides** are both simple **basic hydroxides** which react with acids to form a salt and water.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

- **Aluminium hydroxide** is **amphoteric** so will react with acids and bases:

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$$

- The **other period three hydroxides** each act as **acids** since the **OH group is covalently bonded** to the element.

Period 3 Chlorides and Water

- **Sodium chloride** and **magnesium chloride** are ionic compounds so they **dissolve in water** to form their ions.

- **Aluminium chloride** reacts **violently** with water. Lots of **misty fumes** of hydrogen chloride are produced:

  $$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$

  An **equilibrium** is set up with the product so H^+ ions, and hence HCl, are formed:

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

- **Silicon tetrachloride** reacts with water in the air to produce hydrogen chloride.

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

- **Phosphorus (V) chloride** also reacts violently with cold water to produce hydrogen chloride.

  $$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

  If the water is heated to boiling, the phosphorus (V) chloride reacts further to give phosphoric (V) acid:

  $$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

  The overall reaction in boiling water is:

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

- **Disulfur dichloride** reacts slowly with water to produce a range of products. There are lots of examples of equations that could take place so it is unlikely this will be asked in an exam. Potential products include **HCl, S and H_2S**.

Chemical Bonding in Chlorides and Oxides

In chlorides and oxides, the chemical bonding is **ionic** from sodium to aluminium and **covalent** from silicon to sulfur. This can be deduced from observing the physical and chemical properties of the chloride or oxide being analysed.

Sodium and magnesium form ionic bonds with oxygen and chlorine. Aluminium forms covalent bonds with oxygen and either covalent or ionic bonds with chlorine. Other period 3 elements form simple molecular compounds (covalent). This is because the difference in **electronegativity** between chlorine/ oxygen and the period 3 element decreases across the period. There is sufficient difference in the electronegativity of chlorine/ oxygen and sodium or magnesium to form ions. After aluminium, the difference in electronegativity is **too small** for ions to form.

Bonding and Properties of Chlorides and Oxides

The type of bonding can be deduced using the **physical properties** of group 3 compounds. For example, a high **melting point** means that it is a giant molecular structure, either ionic like NaCl and MgO or covalent like SiO_2.

Chemical properties can also be used to identify the type of bonding:

1. **Chlorides:**
    - Chlorides that dissolve in water to form a solution with a pH close to 7 are ionic.
    - Chlorides that react with water to form an acidic solution and release hydrogen chloride gas are covalent.
2. **Period 3 Oxides:**
    - If a Period 3 oxide forms an acidic solution when it dissolves in water, it is covalent.
    - If it is ionic, it may react with water to form an alkaline solution or may not react with water at all.
3. **General Properties of Oxides:**
    - Ionic oxides are generally basic and react with acids.
    - Covalent oxides tend to be acidic and react with bases.
    - Amphoteric oxides, such as aluminum oxide, are typically ionic with some covalent character.
4. **Electrolysis:**
    - A molten oxide or chloride that can undergo electrolysis must be ionic.

Chemical Periodicity of Other Elements

The chemical properties of an element can be predicted by using knowledge of chemical **periodicity**. Similarly, an unknown element can be identified from information given about its **chemical and physical properties**.