21 Periodicity

GUIDING QUESTIONS

- What are the trends and variations in physical and chemical properties in elements and compounds?
- How can the trends and variations in atomic / physical / chemical properties be explained?
- How can we predict the properties of elements and their compounds?

LEARNING OUTCOMES

Students should be able to:

5(a) recognise variation in the electronic configurations across a Period and down a Group. (Refer to Topic 1 Atomic Structure & Physical Periodicity)

5(b) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity,
  - i. across a Period in terms of shielding and nuclear charge,
  - ii. down a Group in terms of increasing number of electronic shells and nuclear charge

(Refer to Topic 1 Atomic Structure & Physical Periodicity)

5(c) interpret the variation in melting point and in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular) (Refer to Topic 2 Chemical Bonding)

5(d) describe and explain the trend in volatility of the group 17 elements in terms of instantaneous dipole-induced dipole attraction (Refer to Topic 2 Chemical Bonding)

5(e) for elements across the third period:
  - **(i)** state and explain the variation in the highest oxidation number of the elements in oxides (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3) and chlorides (for $NaCl$; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)
  - **(ii)** state and explain the variation in bonding in oxides and chlorides in terms of electronegativity (with the exception of $AlCl_3$)
  - **(iii)** describe the reactions of the oxides with water (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3)
  - **(iv)** describe and explain the acid/base behaviour of oxides (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3) and hydroxides (for $NaOH$; $Mg(OH)_2$; $Al(OH)_3$), including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids
  - **(v)** describe and explain the reactions of the chlorides with water (for $NaCl$; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)
  - **(vi)** suggest the types of structure and bonding present in the oxides and chlorides from observations of their chemical and physical properties

5(f) describe and deduce from $E^\ominus$ values the relative reactivity of elements of:
  - **(i)** Group 2 as reducing agents;
  - **(ii)** Group 17 as oxidising agents

5(g) describe and explain the trend in thermal stability of:
  - **(i)** Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion
  - **(ii)** Group 17 hydrides in terms of bond energies

5(h) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity

5(i) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

REFERENCES

1. Peter Cann & Peter Hughes (2015), *Chemistry*, Hodder Education, Chapters 10 and 11.
2. Martin S. Silberberg, *Chemistry – The Molecular Nature of Matter and Change*, 6th Edition, McGraw-Hill, Chapter 8

LOOKING BACK

In this topic, we will study the trends in chemical properties of elements and their compounds. It is essential to recall knowledge from earlier topics on Atomic Structure & Physical Periodicity and Chemical Bonding: ionisation energy trends and electronegativity have an impact on the types of the bonding found in compounds, and this will in turn affect their physical properties. To explain chemical properties and trends, concepts on redox reactions, electrode potential and acid-base behaviour are also relevant.

1 INTRODUCTION

LO 5(a): Recognise variation in the electronic configurations across a Period and down a Group.

Periodicity is the study of repeating patterns in the physical and chemical properties of the elements in the periodic table.

The arrangement in the periodic table is closely related to the electronic configuration of the elements.

- In the periodic table, elements are arranged in order of <u>increasing proton number</u>.

Prior to 1913, Mendeleev's Periodic Table, which arranged elements according to *atomic mass*, was widely accepted by chemists though there were inconsistencies. Then in 1913, Henry Moseley, using new technology (X-ray electron gun) at that time, showed the link between *atomic number* and element's position in the table, which addressed the inconsistencies and led to the Periodic Table we use today.

Figure 1. Dalton's original table of elements

Table 1. Some trends in Period 3 elements

Element	**Na**	**Mg**	**A*l***	**Si**	**P**	**S**	**C*l***	**Ar**
	metal	metal	metal	metalloid	non-metal	non-metal	non-metal	non-metal
Electronic structure	[Ne] $3s^1$	[Ne] $3s^2$	[Ne] $3s^2 3p^1$	[Ne] $3s^2 3p^2$	[Ne] $3s^2 3p^3$	[Ne] $3s^2 3p^4$	[Ne] $3s^2 3p^5$	[Ne] $3s^2 3p^6$
No. of valence electrons	1	2	3	4	5	6	7	8
Group	1	2	13	14	15	16	17	18
Period	3	3	3	3	3	3	3	3
Electrical conductivity	good conductors			semi-conductor	non-conductors			

- Elements in the <u>same group</u> resemble one another in their chemical properties due to their <u>similar outer electronic configuration</u>. The group number of groups 1 and 2 is the same as the number of <u>valence electrons</u>. The group number of groups to the right of the *d*-block elements can be remembered by adding 10 to the number of valence electrons in each group.

- The <u>period</u> number is the same as the <u>number of quantum shells</u>. Elements in the same period show a periodic change in their chemical and physical properties across the period.

Thus, knowledge of periodicity is useful in understanding and predicting the physical and chemical behaviour of elements.

2 CHEMICAL PROPERTIES OF THE ELEMENTS – Background Information

The following table describes the chemical properties of Period 3 elements and their common uses:

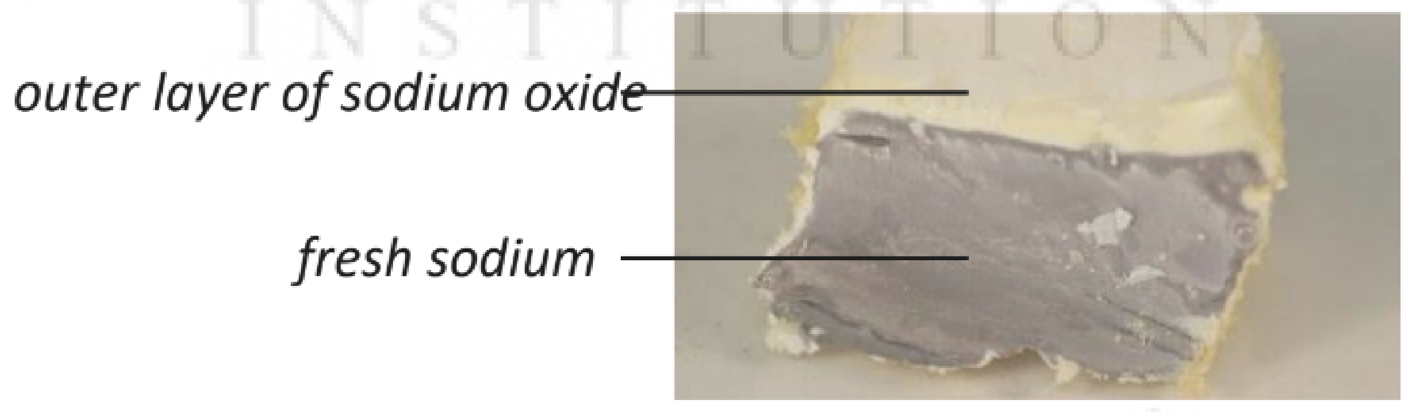
Sodium stored in oil

Na

Sodium

Soft silvery metal

Must be stored in oil to prevent oxidation by air



In air, sodium quickly forms a layer of oxide

Roll of magnesium ribbon

Mg

Magnesium

Often cut into magnesium ribbon strips (left)

Tarnishes (forms oxide) in air, but much less readily than sodium

Magnesium burns with a bright white light, and hence is often used to make fireworks.

Magnesium fireworks

Aluminium foil

A*l*

Aluminium

The metal instantly protects itself in air by forming a thin, but tough, layer of aluminium oxide, Al_2O_3, which is harder than the metal itself.

The toughness of the oxide layer, and the relatively low density of the metal combine to give it an unbeatable strength to weight ratio.

Lightweight sunglasses frame made from aluminium

Aluminium is tough and lightweight, making it perfect for use in the transport and packaging industries.

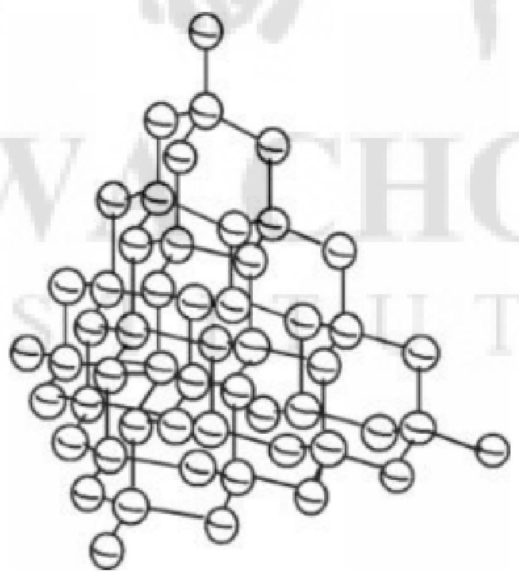
Crystalline silicon has a shiny reflective surface

Si

Silicon

Shiny black metalloid solid

Does not react with air at room temperature.



Structure of silicon

The silicon chip revolutionised electronics

Because silicon is a semiconductor, one of its most important uses is in electronics.

P

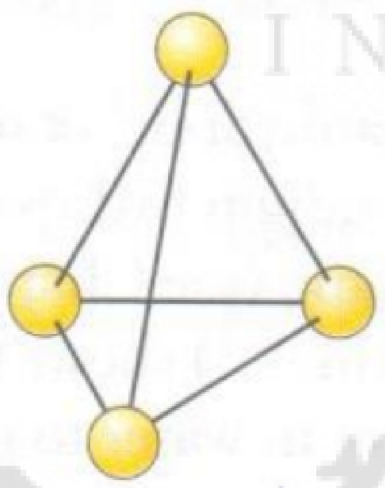
Phosphorus

Phosphorus exists as several allotropes. The most common are white and red phosphorus.

White phosphorus with a corner sliced off

White phosphorus stored under water

White Phosphorus, P_4, is a very reactive waxy solid which generally must be stored under water.

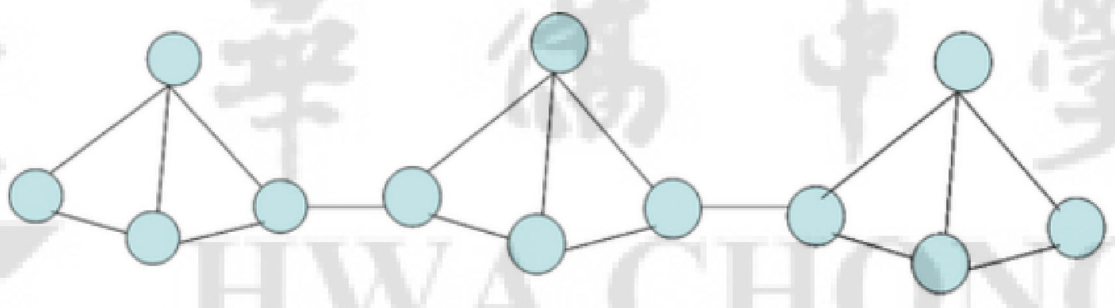


Structure of white phosphorus, P_4

Due to bond angle strain (as the P-P-P bond angle is more acute), it catches fire spontaneously in air.

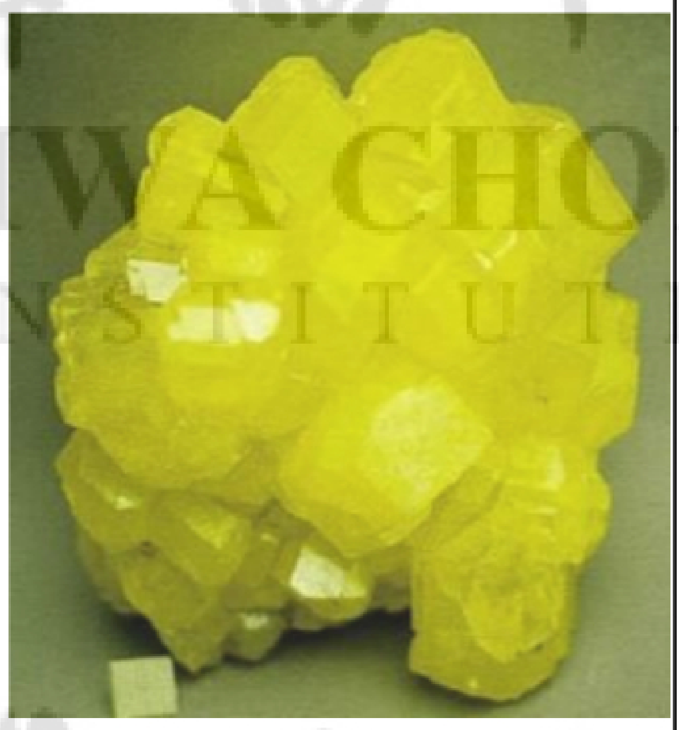
Red Phosphorus, P, is polymeric and appears as a red powder.

Because of the network of linked P atoms, it is much more stable than white phosphorus.



However, it still reacts with air when given enough energy (heating or striking). A common use of red phosphorus is in matches!

Note: In this chapter, we will concentrate on the reactions of white phosphorus P_4.



S

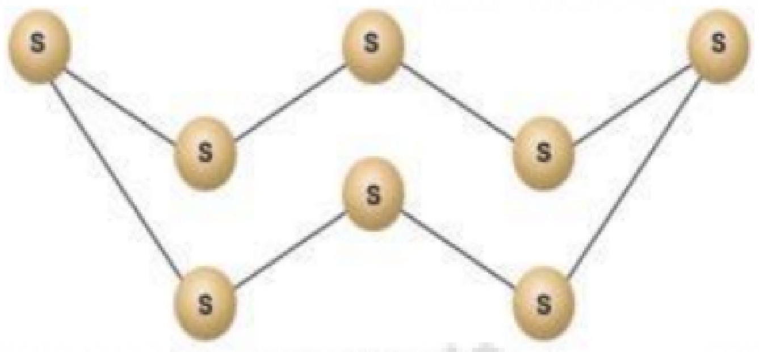
Sulfur

Bright yellow crystalline solid

Pure sulfur is an odourless non-metal.

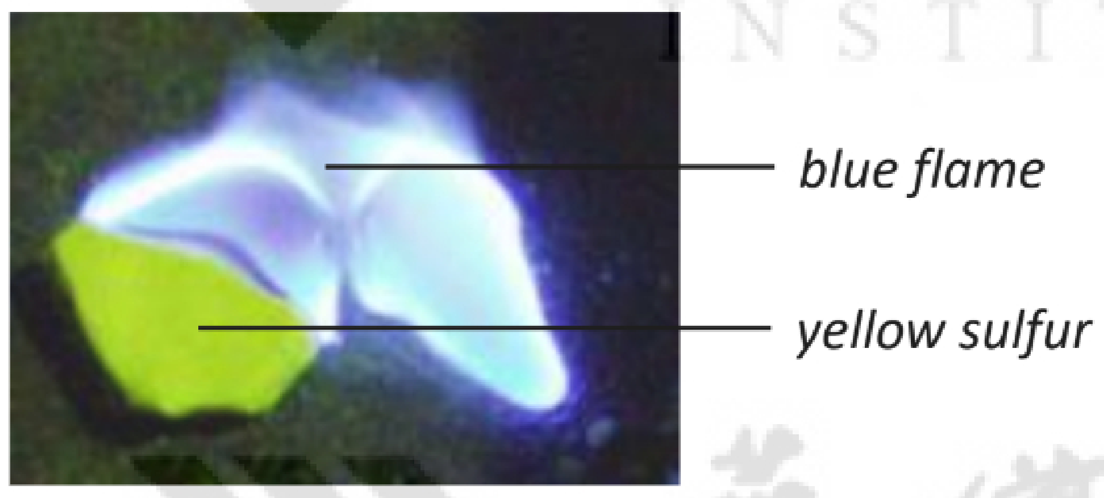
The characteristic smell associated with sulfur is due to its compounds rather than pure sulfur itself.

Elemental sulfur has many different allotropes, but cyclic S_8, is the most common.

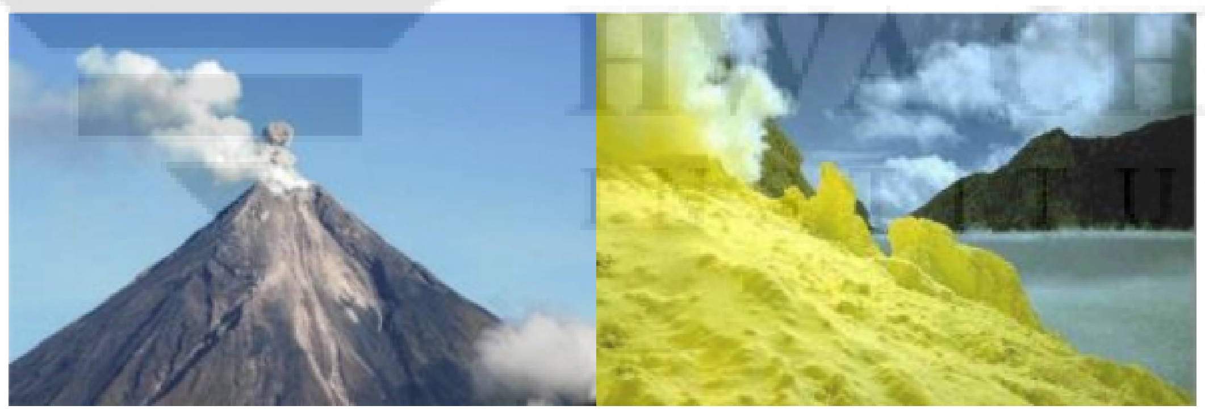


Structure of S_8

Sulfur burns with a blue flame, to form sulfur dioxide



Sulfur combusting



Elemental sulfur can be found near hot springs and volcanoes.

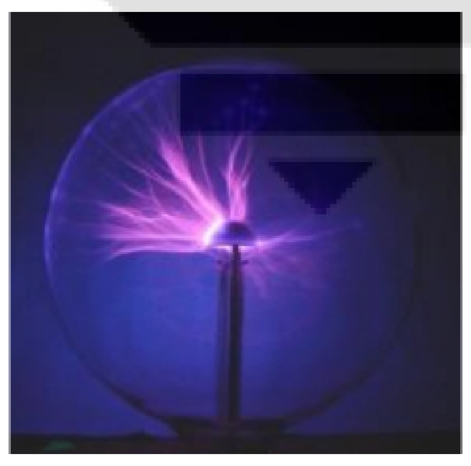
C*l*

Chlorine

Chlorine is a yellow-green toxic gas with a distinctive "bleach" smell.

It exists as diatomic Cl_2 molecules.

Chlorine is a strong oxidising agent that reacts with almost every element to form chlorides. However, it does not react directly with oxygen.



Plasma globe with a pure argon atmosphere

Ar

Argon

Argon is a colourless inert gas. It appears violet when placed in a high voltage electric field (as in the plasma globe to the left).

Self-practice 2.1

1 Which of the following statements about the properties associated with ionic and covalent compounds is correct?

A The only covalent compounds with high melting points are those in which hydrogen bonding occurs.

B Any compound that contains both hydrogen and oxygen atoms in its molecule can form hydrogen bonds.

C Ionic bonds and covalent bonds cannot both occur in the same compound.

D Ionic compounds differ from metals in that ionic compounds do not conduct electricity in the solid state.

[PromoHCI09/P1/Q5]

2 The bond in the compound **XY** is likely to be ionic rather than covalent if

1 **X** is a large cation
2 **Y** is a small anion
3 **X** has a large positive charge

[PromoTJC12/P1/Q17]

3 ***W***, ***X***, ***Y*** and ***Z*** are elements in Period 3.

W has greater electrical conductivity than ***Y*** but lower first ionisation energy than ***X***. ***Y*** has higher melting point than ***W***, and ***Z*** has a greater atomic radius than ***W***.

Based on this information, which of the following is a possible arrangement of these elements in increasing proton number?

A ***W, X, Y, Z***
B ***X, Y, W, Z***
C ***Y, X, Z, W***
D ***Z, W, Y, X***

[PrelimDHS12/P1/Q14]

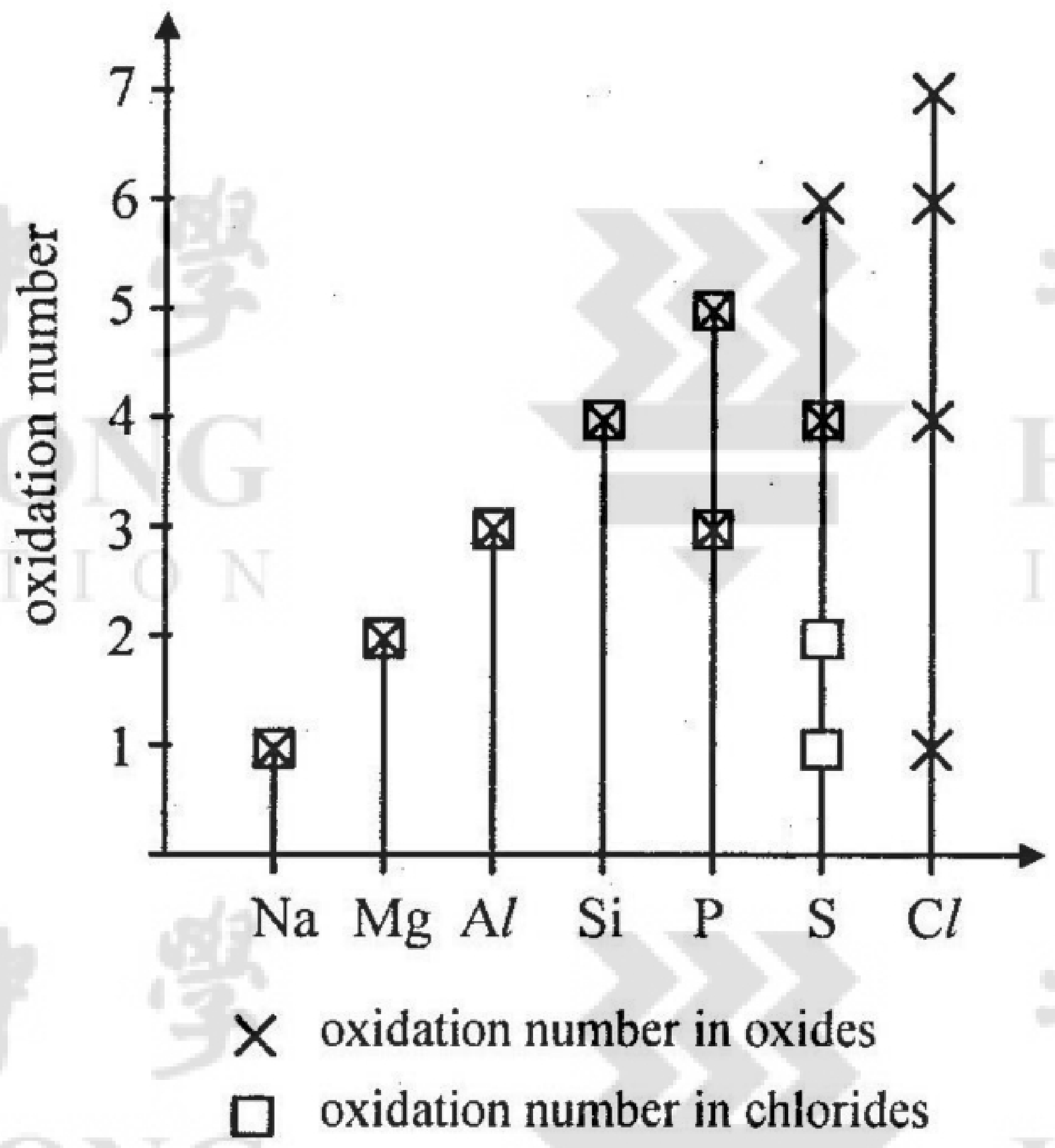
4 State and explain the trend in the electrical conductivity across Period 3 elements, from Na to A*l*.

5 State and explain the trend in the melting point across Period 3 elements, from P to Ar.

3 VARIATION IN OXIDATION NUMBER OF PERIOD 3 OXIDES AND CHLORIDES

LO 5(e)(i): for elements across the third period: state and explain the variation in the highest oxidation number of the elements in oxides (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3) and chlorides (for NaCl; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)

The following diagram and table summarise the oxidation numbers that are found in the oxides and chlorides of Period 3 elements.



Period 3 element	Na	Mg	Al	Si	P		S	
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	P_4O_{10}	SO_2	SO_3
O.N. in oxides	+1	+2	+3	+4	+3	+5	+4	+6
Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	PCl_5		
O.N. in in chlorides	+1	+2	+3	+4	+3	+5		

Note: Sulfur chlorides and chlorine oxides are not in the syllabus.

A few trends can be observed across the period:

- Oxidation numbers of the elements in their oxides are always positive (except for fluorine, where O.N. of F is −1 in F_2O) as oxygen is the most electronegative element other than fluorine.
- From Na to Cl, there is a regular increase in the number of O and Cl atoms that can combine with an atom of the element.
- The maximum positive oxidation number shown by an element often corresponds to the number of valence electrons in an atom of the element.
  - e.g. phosphorus has 5 valence electrons and thus has a maximum oxidation number of +5
- From left to right, the elements show **increasing variation** in possible oxidation numbers: e.g.
  - In their oxides and chlorides, the metals Na, Mg and Al display **only one** possible oxidation number each, corresponding to the loss of all their valence electrons.
  - P, S and Cl exhibit a wider range of oxidation numbers because they can **expand their octets** (by utilising their vacant *d*-orbitals, which are close enough in energy to their valence electrons to be used for chemical bonding as well). The oxidation number thus depends on the number of electrons used for bonding.

Lecture Exercise 3.1

1 Which property of the first six elements of Period 3 (sodium to sulfur) continuously increases numerically?

A atomic radius
B melting point
C first ionisation energy
D maximum oxidation number

4 PROPERTIES OF THE OXIDES

4.1 Structure and bonding of the oxides

LO 5(e)(ii): state and explain the variation in bonding in oxides in terms of electronegativity

The trends in physical properties of the oxides can be explained by the gradual change in their structures and bonding.

Formula of oxide	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_{10}**	**SO_3**
Structure	giant ionic lattice structure (with increasing covalent character from left to right)			giant molecular lattice structure	simple, discrete covalent molecules	
Bonding	strong electrostatic forces of attraction between oppositely-charged ions			strong covalent bonds between atoms	weak intermolecular forces between molecules	

As we move across the period, the bonding of the oxides changes from ionic to covalent.

- This is because the <u>difference in electronegativity</u> between each element and oxygen <u>decreases</u> across the period, hence bonding becomes increasingly covalent. Recall from Topic 2 Chemical Bonding that covalent bonds usually form between atoms of similar electronegativity while atoms with a great difference in electronegativity tend to form ionic bonds. The difference in electronegativity can help us predict if the compound is predominantly ionic or covalent.

4.2 Trend in melting points of the oxides

The trend in melting points of the oxides across the period can be explained by the <u>structure and bonding</u> involved in each oxide.

Formula of oxide	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_{10}**	**SO_3**
Physical state at 25 °C	solid	solid	solid	solid	solid	liquid
Melting point (°C)	1130	2850	2070	1700	sublimes at 360	17

- Na_2O, MgO and Al_2O_3 are all ionic oxides:
  - (Structure) giant ionic lattice with
  - (Bonding) strong electrostatic forces of attraction between oppositely charged ions
  - A large amount of energy is required to overcome the strong ionic bonds ⇒ high m.p.

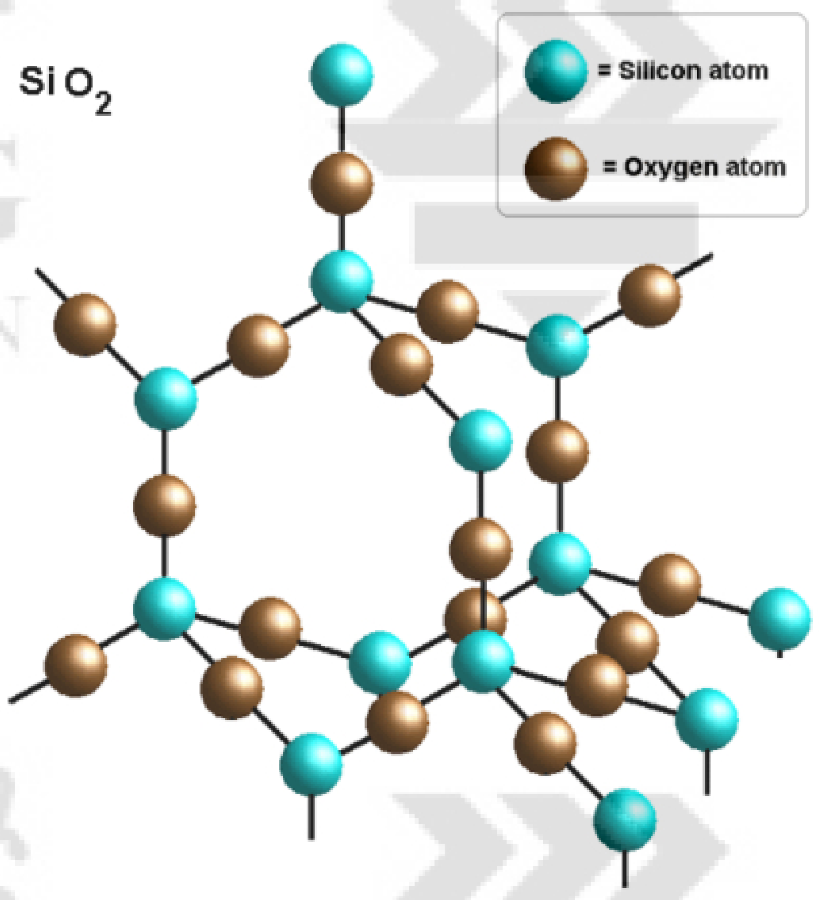
Recall in Topic 2 Chemical Bonding that lattice energy gives an indication of the strength of the ionic bonding – the larger the magnitude of L.E., the stronger the ionic bonding. For ionic compounds, this means a higher m.p.

$$\boxed{\text{Lattice energy } \alpha \ \frac{q_+ \times q_-}{r_+ + r_-}}$$

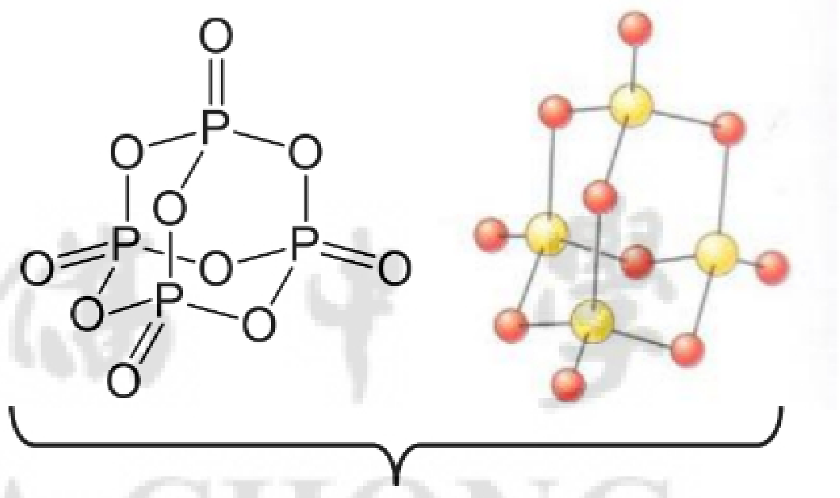
- Melting point of MgO is higher than that of Na_2O:
    - Mg^{2+} has smaller ionic radius and higher charge than Na^+
    - Thus, lattice energy of MgO is much greater in magnitude than that of Na_2O.
    - More energy is required to overcome the electrostatic forces of attraction between Mg^{2+} and O^{2-} than in the Na_2O lattice.

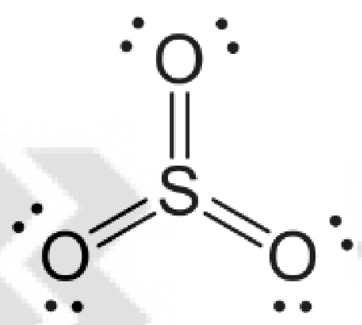
- Melting point of Al_2O_3:
    - Although the lattice energy expression predicts the L.E. of Al_2O_3 to be larger in magnitude than that of MgO, m.p. of Al_2O_3 is actually lower than that of MgO.
    - Possible reason for Al_2O_3 having lower m.p. than MgO:
        - Al^{3+} has very high charge density which can polarise the O^{2-} ion (even though O^{2-} is small and normally not easily polarized) $\Rightarrow$ this confers covalent character to Al_2O_3, which causes magnitude of L.E. to differ from expected.

- Melting point of silicon dioxide (also called silicon(IV) oxide), SiO_2:
    - (Structure) giant molecular structure (resembling that of diamond) with
    - (Bonding) strong covalent bonds between Si and O atoms. Each Si atom is bonded to four O atoms, and each O atom is bonded to two Si atoms.
    - A large amount of energy is required to break the strong covalent bonds $\Rightarrow$ high m.p.



- Oxides of phosphorus and sulfur:
    - (Structure) simple discrete covalent molecules with
    - (Bonding) relatively weak intermolecular dispersion forces between molecules
    - Comparatively less energy is required to overcome these weaker dispersion forces $\Rightarrow$ lower m.p.


Structure of P_4O_{10}



Lecture Exercise 4.1

1 Fibre glass is a mixture of ionic oxides and giant covalent oxides. Which of the following is **unlikely** to be a constituent of fibre glass?

A MgO **B** Al_2O_3 **C** SiO_2 **D** P_4O_{10}

4.3 Acid-base behaviour of the oxides and hydroxides

LO 5(e)(iii): describe the reactions of the oxides with water

(iv): describe and explain the acid/base behaviour of oxides, including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids

(vi): suggest the types of structure and bonding present in the oxides from observations of their chemical and physical properties

From their structure and bonding, the oxides of Period 3 elements can be classified into ionic oxides and covalent oxides. Ionic oxides tend to act as bases whereas covalent oxides act as acids. Oxides of elements that are near the ionic/covalent boundary tend to form amphoteric oxides - i.e. oxides that can act as acids or bases depending on the conditions.

This section will also cover the acid-base behaviour of the three metal hydroxides, $NaOH$, $Mg(OH)_2$ and $Al(OH)_3$.

- **Ionic oxides** contain the O^{2-} ions in their ionic lattice. The O^{2-} ions readily hydrolyse in water to form OH^- ions. Hence, ionic oxides tend to be **basic** in nature:

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$$

- **Covalent oxides** are usually classified as **acidic** oxides because they form acidic solutions when reacted with water, producing H_3O^+ and an oxo-anion (i.e. a negatively charged ion containing the element covalently bonded to a number of oxygen atoms, e.g. SO_4^{2-} and PO_4^{3-}). [Refer to section 4.3.5 on the acidic oxides]

- Aluminium oxide is the only **amphoteric** oxide in Period 3. [Refer to section 4.3.3 for definition of 'amphoteric']

Table 2. Summary list of Period 3 oxides, their bonding and their acid-base nature

	Na	**Mg**	**Al**	**Si**	**P**	**S**
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} P_4O_6	SO_3 SO_2
Bonding	ionic			covalent		
Nature	basic		amphoteric	acidic		

Note: The behaviour and reactions of P_4O_6 and SO_2 are not in the syllabus.

4.3.1 The basic oxides

Sodium oxide and magnesium oxide both react with water and acids, as shown in the table below.

Oxide	Reaction with water	Reaction with acids
Na_2O	**Observation** • appears to dissolve completely in water • vigorous and exothermic reaction, even in cold water • forms a strongly alkaline colourless solution around **pH 13** (depending on concentration) **Equation** $Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)}$	**Observation** • dissolves in acids • reaction is exothermic • reaction produces a salt solution **Equation** $Na_2O_{(s)} + 2H^+_{(aq)} \rightarrow 2Na^+_{(aq)} + H_2O_{(l)}$
MgO	**Observation** • very slow reaction and limited solubility in water, may appear as though nothing is happening • some magnesium hydroxide is formed but it is only sparingly soluble, so not all hydroxide ions formed are released into the solution ⇒ pH is lower than for Na_2O, around **pH 9** **Equations** $MgO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2\,(s)}$ $Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$	**Observation** • dissolves in acids • reaction produces a salt solution **Equation** $MgO_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$

4.3.2 The basic hydroxides

Both sodium and magnesium hydroxides contain the hydroxide ion, OH^-, which is a strong base. Thus, they are basic hydroxides, and can react with acids to form salt solutions in a classic neutralisation reaction.

		Reaction with acids (e.g. dil. hydrochloric acid)	
Hydroxide	**Appearance**	**Observation**	**Equation for the neutralisation**
NaOH	White pellets when solid	Solid dissolves exothermically to give a colourless solution	$NaOH_{(s)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
	Colourless solution when dissolved in water	No visible change, but resultant mixture becomes warmer (exothermic reaction)	$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
$Mg(OH)_2$	White solid/ppt only sparingly soluble in water	Solid/ppt dissolves in acids to give a colourless solution	$Mg(OH)_{2\,(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + 2H_2O_{(l)}$

4.3.3 The amphoteric oxide – Aluminium oxide

Aluminium oxide is an ionic oxide containing Al^{3+} and O^{2-} ions. However, the high charge density of the Al^{3+} ion gives it great polarizing power, allowing the O^{2-} ion to be slightly polarized, despite its small size. This confers some covalent character to the oxide.

This mixture of ionic and covalent character allows Al_2O_3 to display both basic and acidic properties - i.e. it is amphoteric.

Oxide	Reaction with water	Reaction with acids	Reaction with strong bases (sodium hydroxide)
Al_2O_3	**Observation** No reaction in water (insoluble)	**Observation** • dissolves in acids to form a salt solution, with Al^{3+} as the cation **Equation** when reacting as a basic oxide: $Al_2O_{3\,(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$	**Observation** • dissolves in **excess** base to form a salt solution with the Al being part of the anion, the colourless aluminate complex ion $[Al(OH)_4]^-$ **Equation** when reacting as an acidic oxide: $Al_2O_{3\,(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow \underbrace{2[Al(OH)_4]^-_{(aq)}}_{\text{aluminate ion}}$

4.3.4 The amphoteric hydroxide – Aluminium hydroxide

Just like aluminium oxide, aluminium hydroxide is also amphoteric.

- With acids, it reacts just like sodium and magnesium hydroxides, dissolving to form a colourless salt solution of the metal cation, Al^{3+}.
- With strong bases like sodium hydroxide, the hydroxide shows its acidic nature and reacts to form the aluminate anion.

Hydroxide	Appearance	Reaction with acids	Reaction with strong bases (sodium hydroxide)
$Al(OH)_3$	White solid/ppt insoluble in water	**Observation** • dissolves readily in acids to form a colourless salt solution, with Al^{3+} as the cation **Equation** $Al(OH)_{3\,(s)} + 3HCl_{(aq)} \rightarrow \underbrace{AlCl_{3(aq)}}_{\text{salt solution}} + 3H_2O_{(l)}$	**Observation** • dissolves in **excess** strong base to form the colourless aluminate complex ion **Equation** $Al(OH)_{3\,(s)} + NaOH_{(aq)} \rightarrow \underbrace{Na[Al(OH)_4]_{(aq)}}_{\text{salt solution}}$

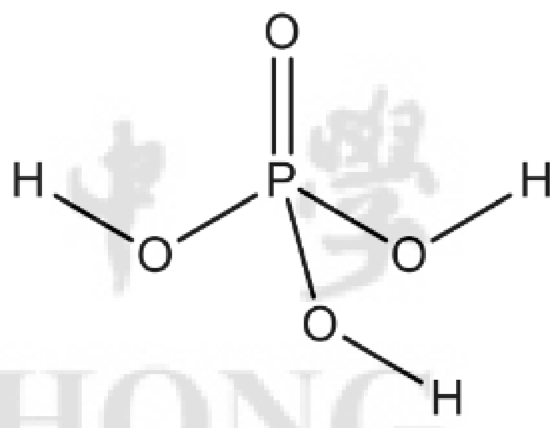
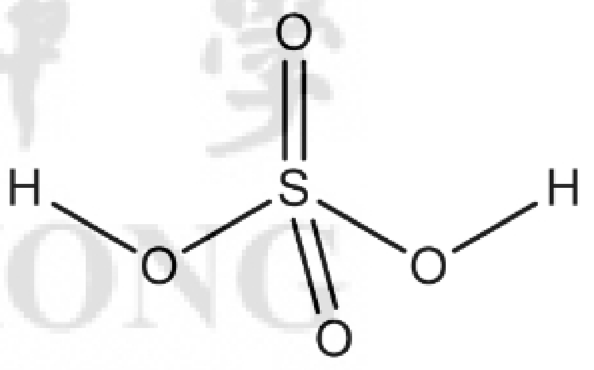
4.3.5 The acidic oxides

As we move across the period, the electronegativity difference between each element and oxygen becomes too small for ionic bonds to form. The remainder of the oxides in Period 3 are thus all covalent in nature.

- Silicon dioxide, SiO_2, is a macromolecular (i.e. giant covalent) oxide that does not contain the O^{2-} ion and hence shows no basic properties at all. It is, however, weakly acidic in nature, and may react with strong bases, usually requiring more vigorous conditions to help in breaking up the macromolecular lattice (e.g. higher concentrations, temperatures, or pressures).

Oxide	Reaction with water	Reaction with strong bases
SiO_2	**Observation** • does not dissolve in/react with water	**Observation** • no reaction with hot aqueous bases (e.g. NaOH) under laboratory conditions • usually requires hot and concentrated strong bases before reaction proceeds • a solution of the silicate salt, SiO_3^{2-}, is formed **Equation** $SiO_{2\,(s)} + 2\,OH^-_{(conc)} \xrightarrow[\Delta]{} SiO_3^{2-}{}_{(aq)} + H_2O_{(l)}$ silicate ion (colourless)

- The oxides of phosphorus and sulfur (and even those of chlorine, though not in the syllabus), are all simple covalent oxides which readily react with water to form acidic solutions.

Oxide	Reaction with water	Reaction with strong bases
P_4O_{10}	phosphorus(V) oxide **Observation** • reacts violently with water to give an acidic solution of H_3PO_4 • forms a fairly strongly acidic solution around **pH 2** (depending on concentration) Phosphoric(V) acid, H_3PO_4, is a triprotic acid, slightly weaker than H_2SO_4. Structure of an undissociated molecule of H_3PO_4:  **Equation** $P_4O_{10\,(s)} + 6\ H_2O_{(l)} \rightarrow 4\ H_3PO_{4\,(aq)}$	**Observation** • dissolves in strong bases to form a salt solution **Equation** if excess OH^- is added: $P_4O_{10\,(s)} + 12\ OH^-_{(aq)} \rightarrow 4\ PO_4^{3-}{}_{(aq)} + 6\ H_2O_{(l)}$
SO_3	Sulfur trioxide **Observation** • violent and very exothermic reaction in water, producing a very acidic mist of H_2SO_4 droplets • forms a strongly acidic solution around **pH 1** (depending on concentration) The sulfuric acid formed, also known as sulfuric(VI) acid, is a strong dibasic acid, which ionises completely in water. Structure of an undissociated molecule of H_2SO_4:  **Equation** $SO_{3\,(l)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)}$ strongly acidic solution	**Observation** • reacts directly with bases to form salt solutions **Equation** $SO_{3\,(l)} + 2\ OH^-_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + H_2O_{(l)}$

4.4 Summary of the properties of oxides across Period 3

The following table summarises the trends in the Period 3 oxides (in their highest oxidation states):

Formula of oxide	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_{10}**	**SO_3**
Oxidation number	+1	+2	+3	+4	+5	+6
Physical state at 25 °C	solid	solid	solid	solid	solid	liquid
Melting point (°C)	1130	2850	2070	1700	sublimes at 360	17
Bonding & structure	giant ionic lattice structure with strong electrostatic forces of attraction between oppositely-charged ions (with increasing covalent character from left to right)			giant molecular structure, covalent bonding	simple, discrete covalent molecules with relatively weak dispersion forces between molecules	
Acidic/basic nature	basic		ampho-teric	acidic		
Reaction with water	soluble reacts to form strongly basic NaOH	sparingly soluble reacts to form weakly basic $Mg(OH)_2$	Insoluble in water large amount of energy required to break lattice structures		soluble reacts to form fairly acidic H_3PO_4	soluble reacts to form strongly acidic H_2SO_4
Approx. pH* of aqueous solution *assuming similar initial concentrations of the oxide	13	9	7	7	2	1

Lecture Exercise 4.2

1 **X**, **Y** and **Z** are elements in the same short period of the Periodic Table. The oxide of **X** is amphoteric, the oxide of **Y** is basic, and the oxide of **Z** is acidic. What is the order of increasing atomic (proton) number for these elements?

A XYZ **B** XZY **C** YXZ **D** YZX

2 Based on your knowledge of periodicity and Period 3 elements, predict the nature of Cl_2O_7, an oxide of chlorine.

A Basic **B** Acidic **C** Amphoteric **D** Neutral

3 Which of the following oxides produces the strongest acid when treated with water?

A SO_3 **B** Al_2O_3 **C** P_4O_{10} **D** SiO_2

4 A mixture of the oxides of two elements of the third period is dissolved in water. The solution remained approximately neutral.
What could be the constituents of the mixture?

A Al_2O_3 and MgO
B Na_2O and MgO
C Na_2O and P_4O_{10}
D SO_3 and P_4O_{10}

[J03/P1/Q13]

5 Consider the sequence of oxides Na_2O, SiO_2, P_4O_{10}. Which of the following factors decreases from Na_2O to SiO_2 and also from SiO_2 to P_4O_{10}?

A melting point
B covalent character
C pH when mixed with water
D solubility in aqueous alkali

5 PROPERTIES OF THE CHLORIDES

LO 5(e)(ii): state and explain the variation in bonding in chlorides in terms of electronegativity (except for $AlCl_3$)
(v): describe and explain the reactions of the chlorides with water (for $NaCl$; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)
(vi): suggest the types of structure and bonding present in the chlorides from observations of their chemical and physical properties

5.1 Structure and bonding of the chlorides

The trends in physical properties of the chlorides can also be explained by the gradual change in their structure and bonding. Like the oxides, the bonding of the chlorides changes from ionic to covalent across the period.

Formula of chloride	**$NaCl$**	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_5**
Structure	giant ionic lattice structure		simple discrete covalent molecules *(in vapour phase)*	simple discrete covalent molecules	simple discrete covalent molecules *(in vapour phase)*
Bonding	strong electrostatic forces of attraction between oppositely-charged ions		weak dispersion forces between molecules		

Again, this is because the <u>electronegativity difference</u> between each element and chlorine <u>decreases</u> across the period, hence bonding becomes increasingly covalent.

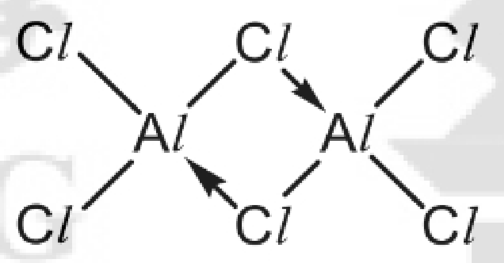
5.2 Trend in melting points of the chlorides

As for the oxides, the trend in melting points of the chlorides across the period can be explained by their <u>structure and bonding</u>.

Formula of chloride	**$NaCl$**	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_5**
Physical appearance at 25 °C	solid	solid	solid	liquid	solid
Melting point (°C)	801	714	sublimes at ~180	–70	sublimes at ~160

- $NaCl$ and $MgCl_2$:
    - white crystalline solids at room temperature
    - (Structure) giant ionic lattice with
    - (Bonding) strong electrostatic forces of attraction between oppositely charged ions
    - A large amount of energy is required to overcome the strong ionic bonds ⇒ high m.p.

- Aluminium chloride:
    - very pale yellow powder at room temperature
    - In the vapour phase, aluminium chloride is simple molecular in structure, forming gaseous Al_2Cl_6 dimers (which involve dative bonding):



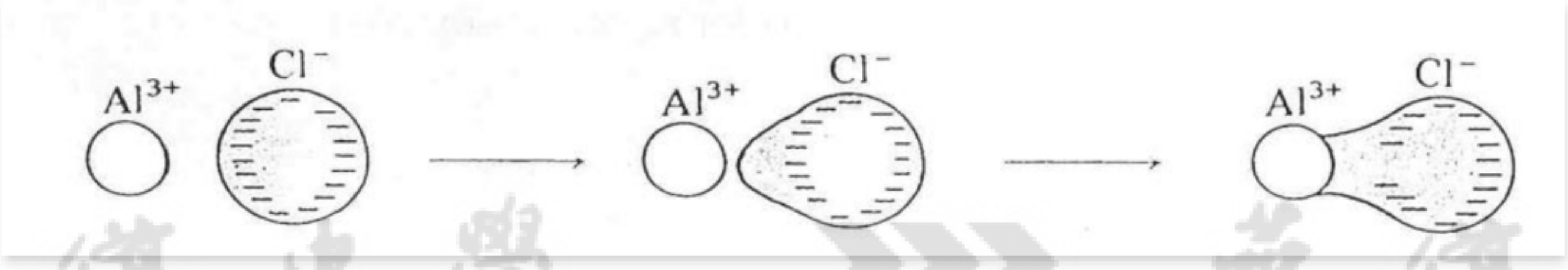
Al_2Cl_6 dimer

- ○ In the vapour phase, there exists an equilibrium between Al_2Cl_6 dimers and $AlCl_3$ monomers. As the temperature increases, the position of the equilibrium shifts more to the right, favouring the monomers.

$$Al_2Cl_{6\,(g)} \rightleftharpoons 2AlCl_{3\,(g)}$$

For your information: Is aluminium chloride really a simple covalent compound?

In the solid state, $AlCl_3$ actually has an ionic lattice structure with a large amount of covalency. This covalency is due to the very high charge density of the Al^{3+} ion (small ionic radius and high charge) which is able to polarise the large electron cloud of nearby Cl^- ions.



Just below 180 °C, the solid expands and $AlCl_3$ loses all ionic character, converting to discrete Al_2Cl_6 gas molecules with comparatively weaker dispersion forces between them, causing the solid to suddenly vaporise (i.e. it sublimes).

Aluminium chloride is said to have a borderline type of bonding, somewhere in between that of purely ionic and purely molecular compounds.

- Silicon tetrachloride, $SiCl_4$:
  - ○ It is a colourless fuming liquid at room temperature
  - ○ (Structure) simple discrete covalent molecules with
  - ○ (Bonding) relatively weak intermolecular forces between molecules
  - ○ Comparatively less energy is required to overcome these weaker forces ⇒ lower m.p.

- phosphorus(V) chloride, PCl_5:
  - ○ off-white to pale yellow powder at room temperature
  - ○ PCl_5 is considered to have a simple molecular structure and can largely be treated as such in the context of A-level chemistry.

For your information: Why is PCl_5 a solid at room temperature?

At room temperature, when in the solid state, PCl_5 self-ionises, causing it not to melt as expected due to stronger ionic interactions:

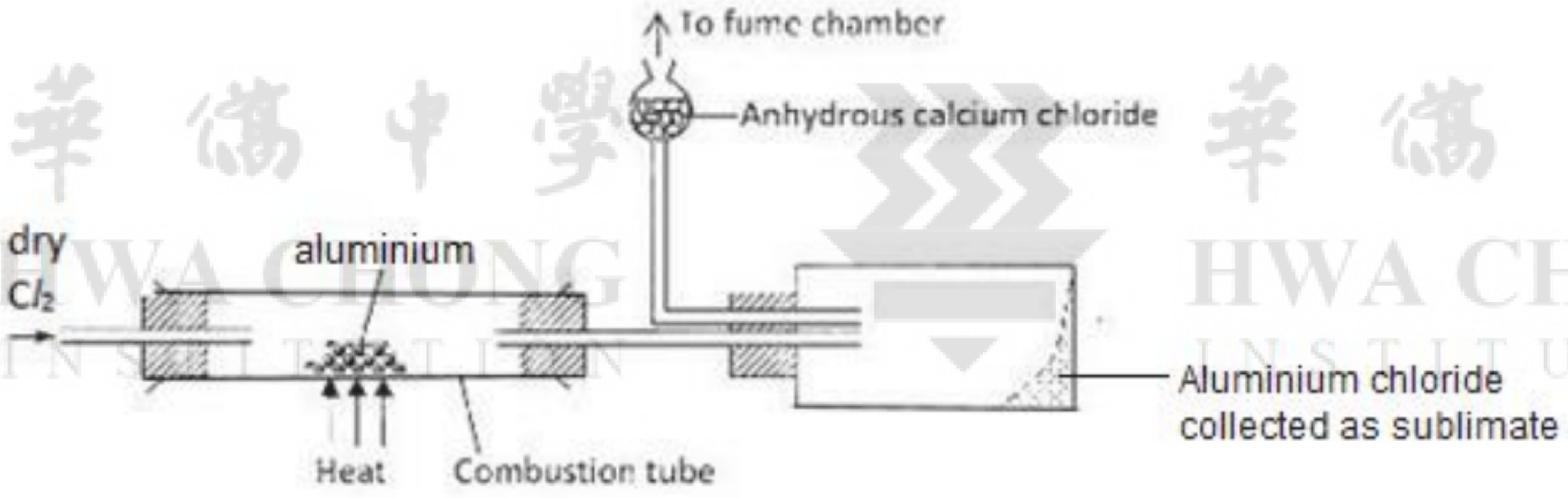
$$PCl_5 + PCl_5 \rightarrow PCl_4^+ + PCl_6^-$$

At around 160 °C, the ions convert back to simple molecular PCl_5 with relatively weaker intermolecular dispersion forces. Because these attractions are easier to overcome, PCl_5 then sublimes.

Laboratory Situations – Preparation of Inorganic Compounds: e.g. Aluminium chloride

You may be required to plan experiments to prepare and purify inorganic substances. The separation and purification techniques used in Organic Chemistry are also applicable for inorganic compounds: filtration, extraction, distillation, recrystallization, and melting point determination.

Using aluminium chloride as an example, here is a fully labelled diagram of a laboratory set up used to produce, purify and collect an inorganic compound. Of course, the physical state and properties of the desired compound should be considered when designing the experiment.



Ensuring a moisture-free environment

Drying the chlorine gas before feeding it through the system, and adding a calcium chloride guard tube at the exit point help to ensure that the environment in which the aluminium chloride is prepared is free from water. This is particularly important because aluminium chloride reacts very readily with water.

Anhydrous calcium chloride is very hygroscopic (i.e. easily absorbs moisture from air), hence very useful as a desiccant (i.e. a drying agent). Placing some in a guard tube allows for absorption of any moisture from the air, particularly when the set-up cools (which causes some air to enter the set up via contraction).

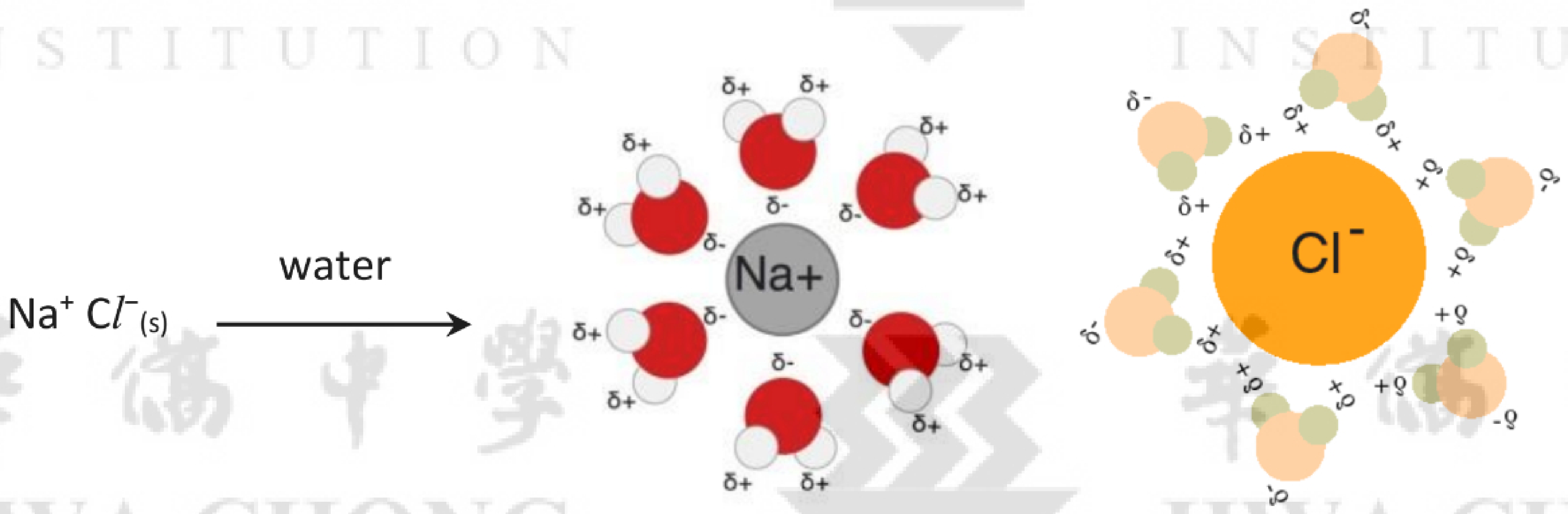
How are gases like chlorine 'dried'?

It is possible to dry chlorine gas by bubbling the supply of chlorine through concentrated sulfuric acid, which readily absorbs any moisture in the gas supply.

5.3 Reactions of the chlorides with water

On the whole, all chlorides of Period 3 elements appear to dissolve in water.

- In the case of the ionic chlorides, their ions get solvated, and form favourable ion-dipole interactions with the polar water molecules. We refer to the solvated ions as hydrated ions.
- Recall that the chloride ion, being the conjugate base of the strong acid HCl, is a very poor base which does not react with water. Hence, it will not be responsible for any deviations from neutral pH.
- Depending on their charge density, the hydrated metal cations formed may undergo **partial hydrolysis** in water.

Chloride	**Reaction with water**
$NaCl$	**Observation with equation** • dissolves in water to form a colourless solution of neutral pH $NaCl_{(s)} + aq \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$ **Explanation** • Na^{+} has low charge density, and hence does not react with water molecules (no hydrolysis). The solution thus remains neutral at **pH 7**. 
$MgCl_2$	**Observation with equation** • dissolves in water to form a colourless solution of slightly acidic pH $MgCl_{2(s)} + 6H_2O_{(l)} \rightarrow [Mg(H_2O)_6]^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$ $[Mg(H_2O)_6]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Mg(H_2O)_5OH]^{+}_{(aq)} + H_3O^{+}_{(aq)}$ **Explanation** • Due to the higher charge density of Mg^{2+} compared to Na^{+}, the hydrated magnesium ion undergoes slight hydrolysis to form a very weakly acidic solution of around **pH 6.5**. • The above equilibrium lies very much to the left. Nonetheless, enough H_3O^{+} is produced to lower the pH away from neutral.

Chloride	**Reaction with water**
$AlCl_3$	**Observation with equations** **1. Reaction in a limited amount of water** When a few drops of water are added to solid $AlCl_3$, steamy white fumes of HCl are evolved and a white solid remains, which is insoluble in water. $AlCl_{3\,(s)} + 3\,H_2O_{(l)} \rightarrow \underset{\text{white solid}}{Al(OH)_{3(s)}} + \underset{\text{steamy white fumes}}{3\,HCl_{(g)}}$ **2. Reaction in a large amount of water** In an excess of water, $AlCl_3$ dissolves to form a colourless solution of acidic pH. Al^{3+} forms a complex ion with 6 water molecules, as shown below. $AlCl_{3(s)} + 6\,H_2O_{(l)} \rightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3\,Cl^-_{(aq)}$ $[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$ Due to the very high charge density of Al^{3+}, the O–H bonds in the H_2O ligands are sufficiently polarised, weakened and break readily to donate a proton. The hydrated aluminium complex can undergo hydrolysis to a further extent than for Mg^{2+}(aq), resulting in a distinctly acidic solution around **pH 3.** **3. Acidic behaviour of Al^{3+}(aq)** • Adding a controlled amount of OH^- ions to an aqueous solution of Al^{3+} can further deprotonate the water ligands, until a white ppt of aluminium hydroxide is formed: $[Al(H_2O)_5OH]^{2+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [Al(H_2O)_4(OH)_2]^+_{(aq)} + H_2O_{(l)}$ $[Al(H_2O)_4(OH)_2]^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons \underset{\text{white ppt}}{[Al(H_2O)_3(OH)_3]_{(s)}} + H_2O_{(l)}$ • If an excess of OH^- ions is added, the white ppt dissolves to form a colourless solution with the formation of the aluminate ion: $[Al(H_2O)_3(OH)_3]_{(s)} + OH^-_{(aq)} \rightleftharpoons \underset{\text{aluminate}}{[Al(OH)_4]^-_{(aq)}} + 3\,H_2O_{(l)}$ N.B. The aluminate complex is sometimes written as $[Al(H_2O)_2(OH)_4]^-$, the octahedral complex. However, this is rather unstable, quickly forcing out the 2 water molecules and converting to the tetrahedral $[Al(OH)_4]^-$. • A solution of Al^{3+} is usually acidic enough to react with sodium carbonate and produce effervescence of CO_2 gas and the white ppt of aluminium hydroxide. $2\,[Al(H_2O)_6]^{3+}_{(aq)} + 3\,CO_3^{2-}{}_{(aq)} \rightarrow 2\,\underset{\text{white ppt}}{[Al(H_2O)_3(OH)_3]_{(s)}} + 3\,H_2O_{(l)} + \underset{\text{effervescence}}{3\,CO_{2(g)}}$ Refer to Section 3.1.4 in Topic 15 Acid-Base Equilibria for more details on hydrolysis caused by metal ions with high charge density.

- The remainder of the chlorides undergo **complete hydrolysis** in water to form **strongly acidic** solutions due to the **HCl** formed.

Chloride	Reaction with water
$SiCl_4$ / PCl_5	**Observation** • violent reaction with water producing fumes of HCl gas Note that even if left exposed to moist air, fumes of HCl will be observed. ▪ ∴ these chlorides must be kept in air-tight containers • If water is added in large excess, the HCl fumes may not be observed as they mostly dissolve in the water, forming a strongly acidic solution (**pH 1**) containing hydrochloric acid. **Equations** Complete hydrolysis occurs in each case, i.e. these chlorides react with water irreversibly. $SiCl_{4(l)} + 4\ H_2O_{(l)} \rightarrow \underset{\text{hydrated silicon dioxide*}}{SiO_2.2H_2O_{(s)}} + 4\ HCl_{(aq)}$ $PCl_{5(s)} + 4\ H_2O_{(l)} \rightarrow \underset{\text{phosphoric(V) acid}}{H_3PO_{4(aq)}} + 5\ HCl_{(aq)}$ • Upon dropwise addition of water (or when exposed to moist air), phosphorus(V) chloride tends to produce phosphorus oxychloride, $POCl_3$, instead: $PCl_{5(s)} + H_2O_{(l)} \rightarrow POCl_{3(l)} + 2\ HCl_{(g)}$ **Recall**: This is similar to the reaction when PCl_5 is used as a test for the –OH group in organic chemistry! $PCl_{5(s)} + ROH_{(l)} \rightarrow POCl_{3(l)} + HCl_{(g)} + RCl_{(l)}$

*Note: Hydrated silicon dioxide is sometimes written as $Si(OH)_4$, a misleading notation that leads some to believe it is basic (it's not!), or as H_4SiO_4, in which it looks more like the molecular formula of an acid , which is more accurate here (*orthosilicic acid*, H_4SiO_4, has $pK_{a1}=9.84$, $pK_{a2}=13.2$ at 25 °C *from Wikipedia*). However, silicic acids such as H_4SiO_4 readily lose water to form randomly polymeric silica gel, a form of silicon dioxide, hence the use of the formula $SiO_2.2H_2O$.

5.4 Summary of the properties of chlorides across Period 3

The following table summarises the trends in the Period 3 chlorides (in their highest oxidation states):

Formula of chloride	**$NaCl$**	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_5**
Oxidation number	+1	+2	+3	+4	+5
Physical appearance at 25 °C	solid	solid	solid	liquid	solid
Melting point (°C)	801	714	sublimes at ~180	–70	sublimes at ~160
Boiling point (°C)	1413	1412	-	58	-
Bonding & structure	giant ionic lattice structure with relatively strong electrostatic forces of attraction between oppositely-charged ions		simple discrete covalent molecules with relatively weak dispersion forces between molecules		
Effect of adding chloride to water	soluble does not hydrolyse	soluble hydrolyses slightly	soluble hydrolyses in water to form acidic solutions; HCl fumes may be observed		
Approx. pH of resulting solution	7	6.5	3	1	1

Lecture Exercise 5.1

1 The chloride of element **J** neither reacts with nor dissolves in water. Which of the following could element **J** be?

A Aluminium **C** Magnesium
B Carbon **D** Silicon

2 An element of Period 3 (Na to S) is heated in chlorine. The product is purified and then added to water. The resulting solution is found to be neutral. What is the element?

A Sodium **C** Silicon
B Aluminium **D** Phosphorus

For questions 3 to 6, you may select **more than one** correct option.

3 Which of the following pairs of compounds contains one that is giant ionic and one that is simple molecular?

1 Al_2O_3 and Al_2Cl_6
2 SiO_2 and $SiCl_4$
3 P_4O_{10} and PCl_5

4 Which of the following sets contains two covalent chlorides and two ionic chlorides?

1	$NaCl$	$BaCl_2$	CCl_4	ICl
2	$BeCl_2$	$SiCl_4$	$PbCl_4$	SCl_2
3	$CaCl_2$	$SiCl_4$	PCl_5	SCl_2

5 Why is a solution of aluminium chloride acidic?

1 Chloride ions react with water to form hydrochloric acid.
2 Aluminium ions have a large charge to surface area ratio.
3 The H–O bonds are weaker in $[Al(H_2O)_6]^{3+}$ than in H_2O.

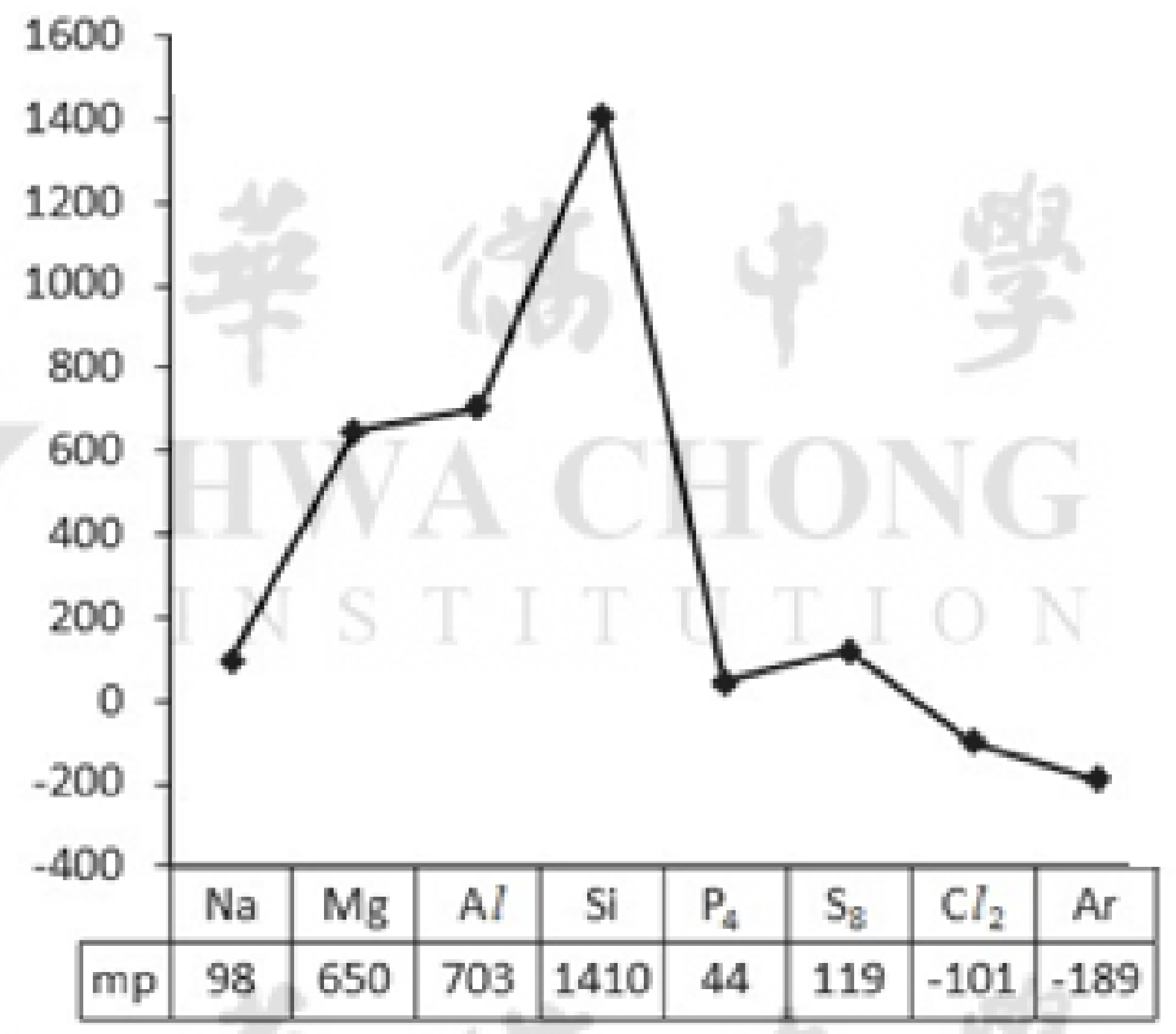
6 Which of the following are correct descriptions of the properties of anhydrous aluminium chloride?

1 It dissolves in benzene to give a solution which conducts electricity.
2 It fumes in moist air due to the formation of hydrogen chloride.
3 In the vapour phase, it has a covalent molecular structure.

6 SUMMARY OF PERIOD 3 TRENDS

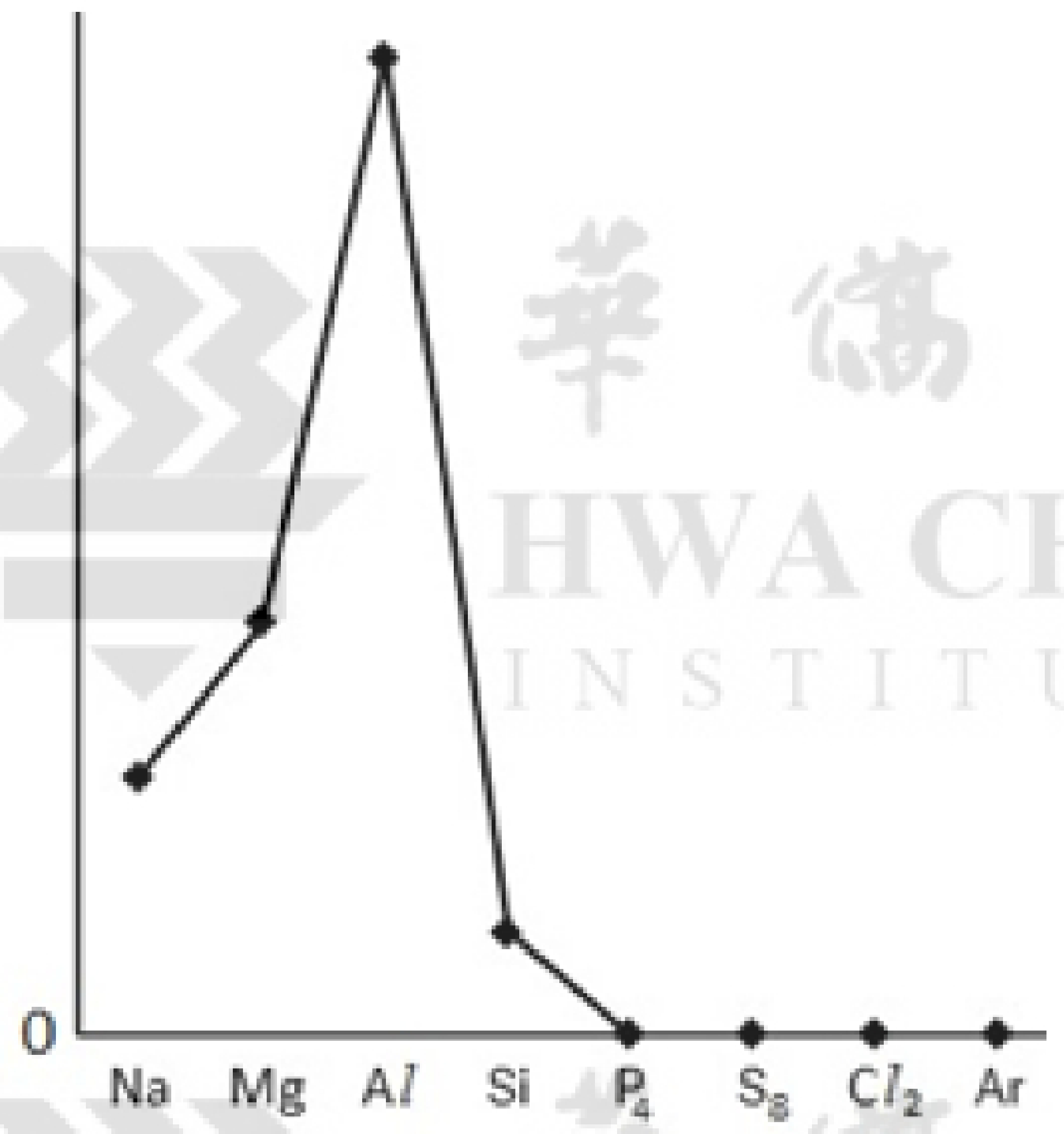
- **Variations in physical properties of the Period 3 elements**

melting point (in °C)



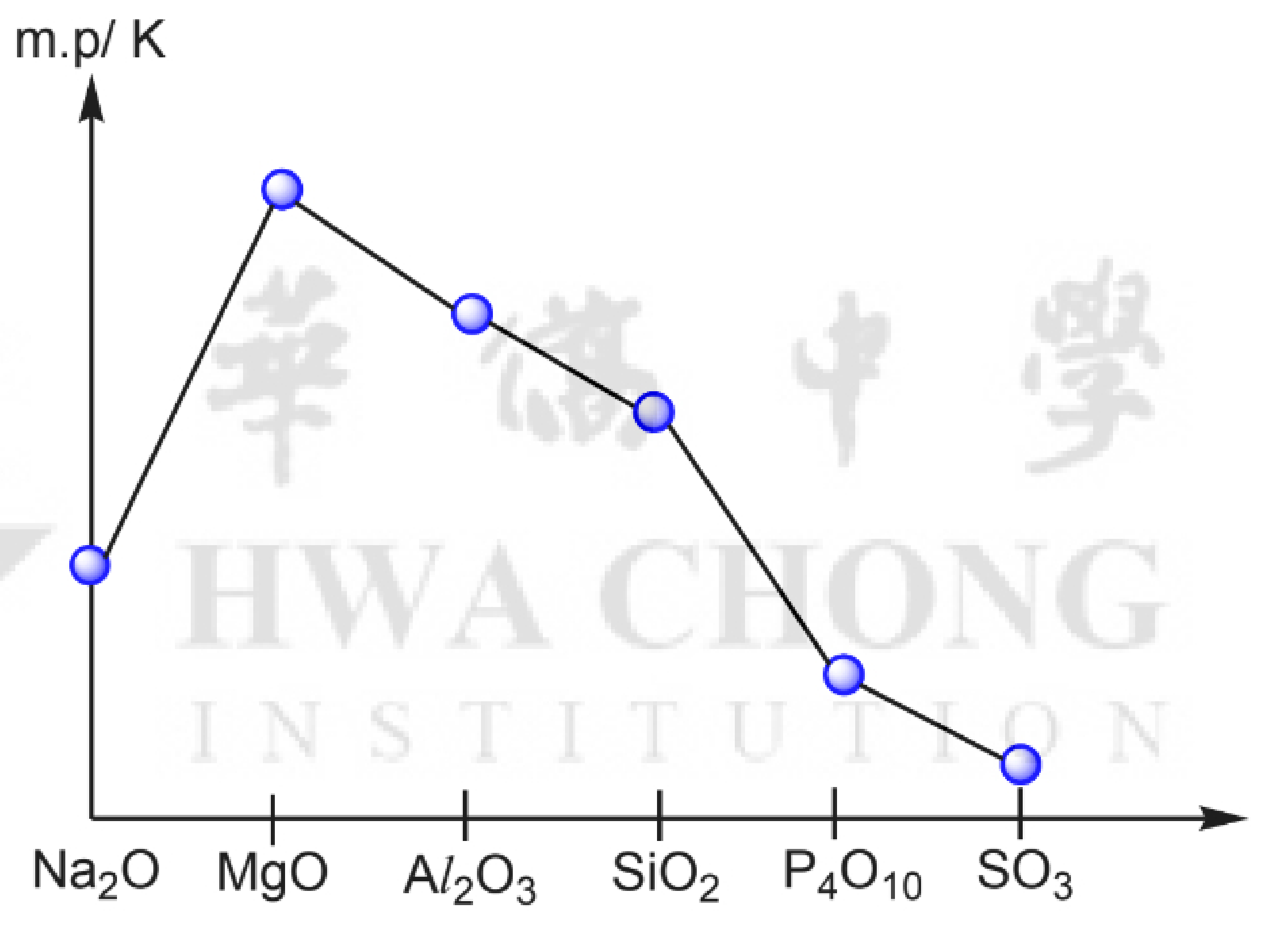
	Na	Mg	Al	Si	P_4	S_8	Cl_2	Ar
mp	98	650	703	1410	44	119	-101	-189

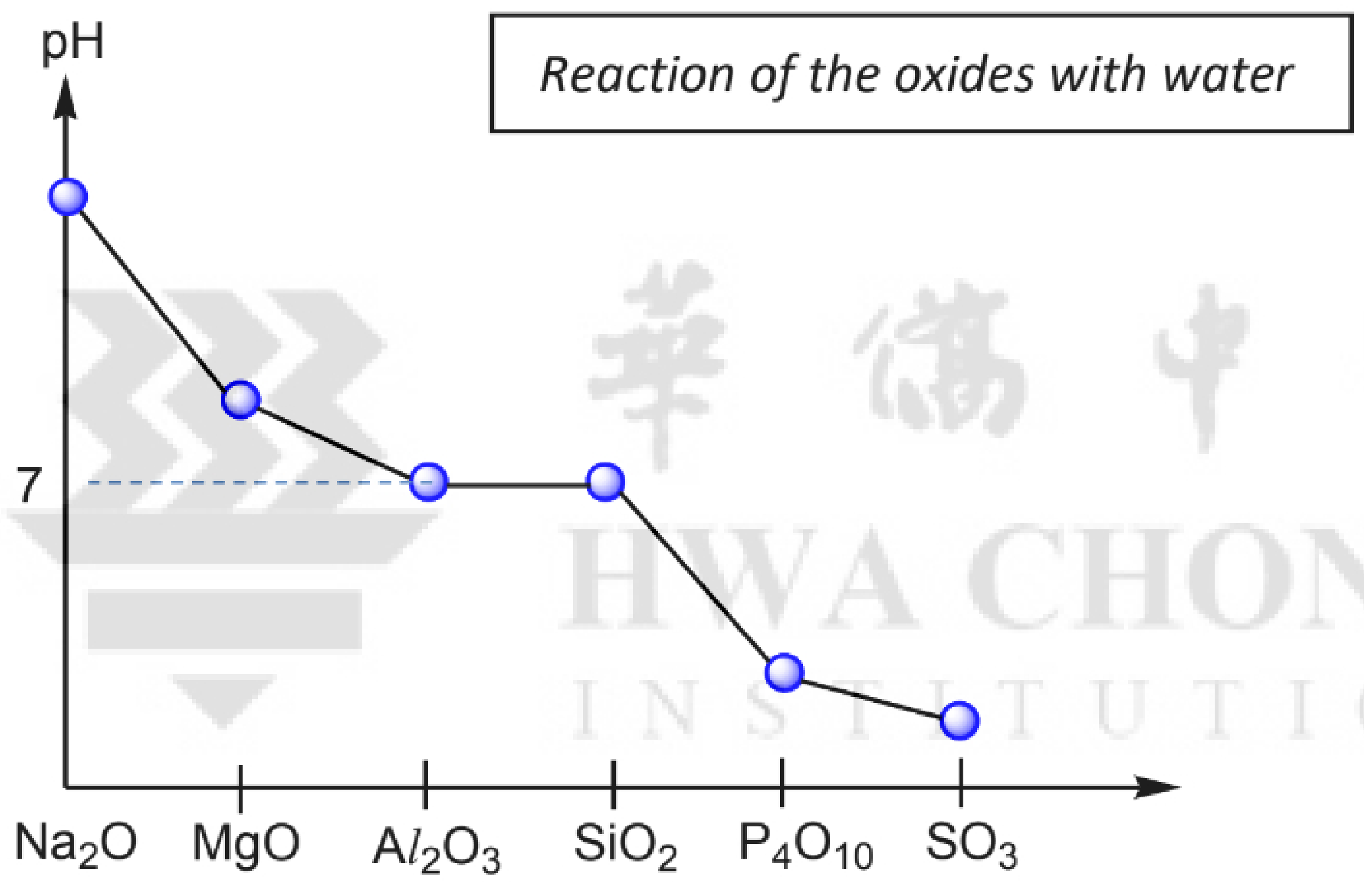
electrical conductivity



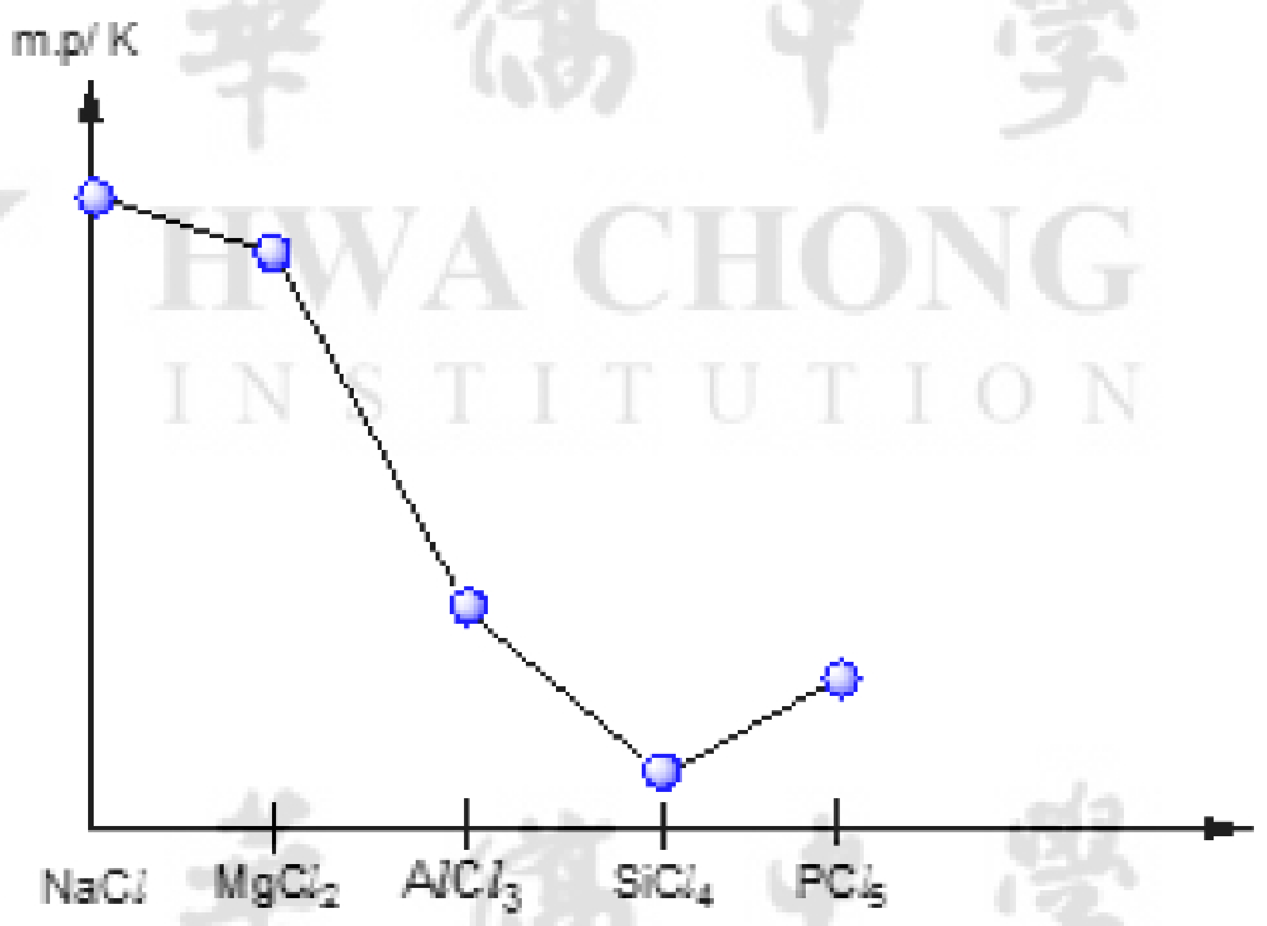
Refer to Topic 2 Chemical Bonding for the explanations of melting point and electrical conductivity variation using concepts of structure and bonding.

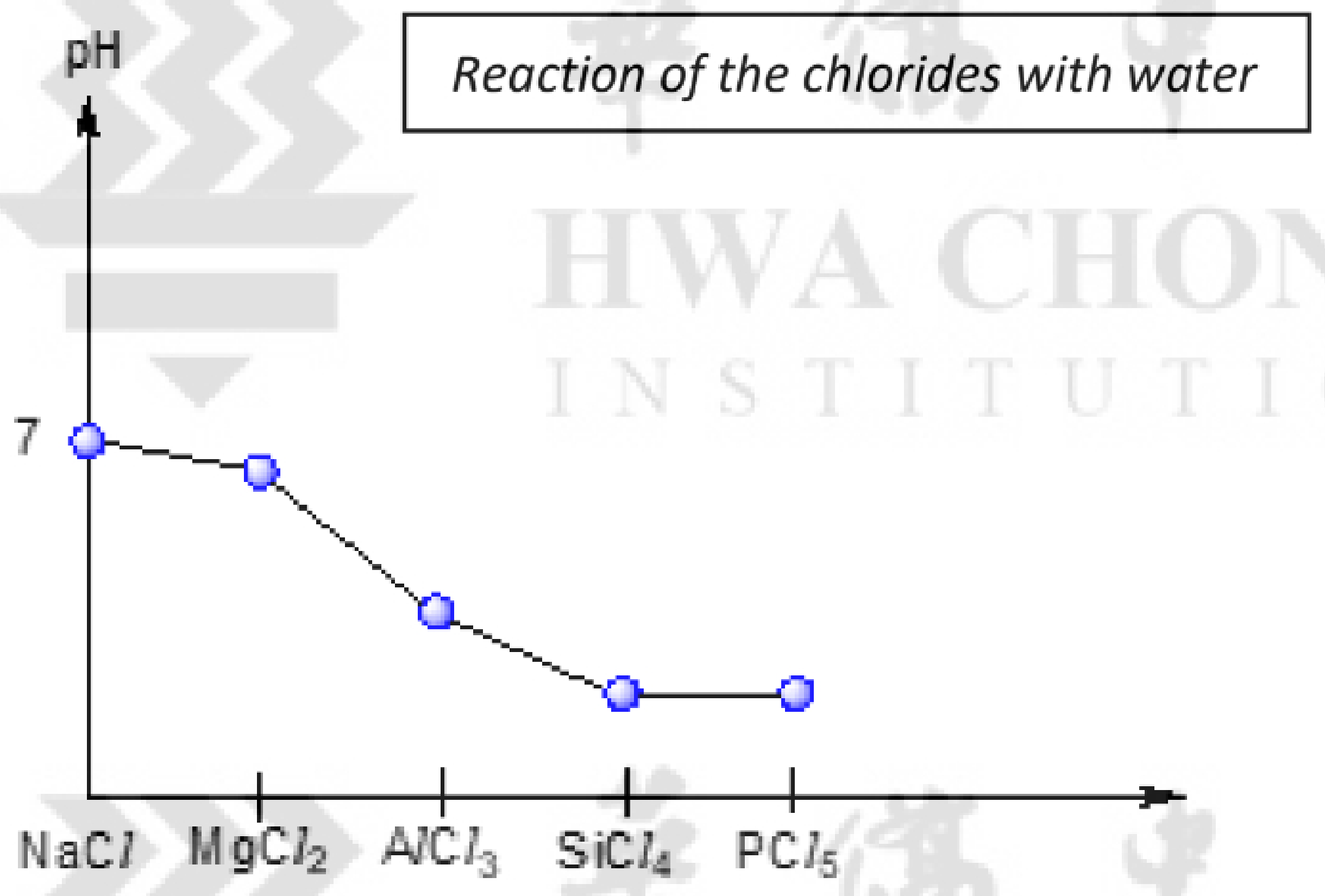
- **Variations in properties of the Period 3 oxides**





- **Variations in properties of the Period 3 chlorides**





7 GROUP 2

LO 5(f)(i): describe and deduce from $E^\ominus$ values the relative reactivity of elements of Group 2 as reducing agents
LO 5(g)(i): describe and explain the trend in thermal stability of Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion

7.1 Relative strength of Group 2 metals as reducing agents

Reactivity of the Group 2 metals **increases** down the group. As atomic radii increase, the metal atoms lose their electrons more readily (1st and 2nd ionisation energies decrease) going down the group. So, they form M^{2+} cations more easily.

Therefore, **reducing power** of the group 2 metals **increases** (tendency to be oxidised increases) down the group.

This is illustrated in the **increasingly negative** $E^\ominus$ values down the group.

Table 3. Standard electrode potential values of Group 2 metals

Element	Standard electrode potential, $E^\ominus$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90

7.2 Thermal stability of Group 2 carbonates

Group 2 carbonates are **unstable** towards heat. Thermal decomposition gives stable oxides.

$$\boxed{MCO_3(s) \rightarrow MO(s) + CO_2(g)}$$

Table 4. Decomposition temperatures of Group 2 carbonates

Element	Decomposition Temperature of carbonate / °C
Mg	400
Ca	900
Sr	1280
Ba	1360

Group 2 carbonates become **more thermally stable** down the group. The ones lower in the group need to be heated more strongly before they will decompose, i.e. the ease of decomposition decreases down the group, hence they will have a **higher decomposition temperature**.

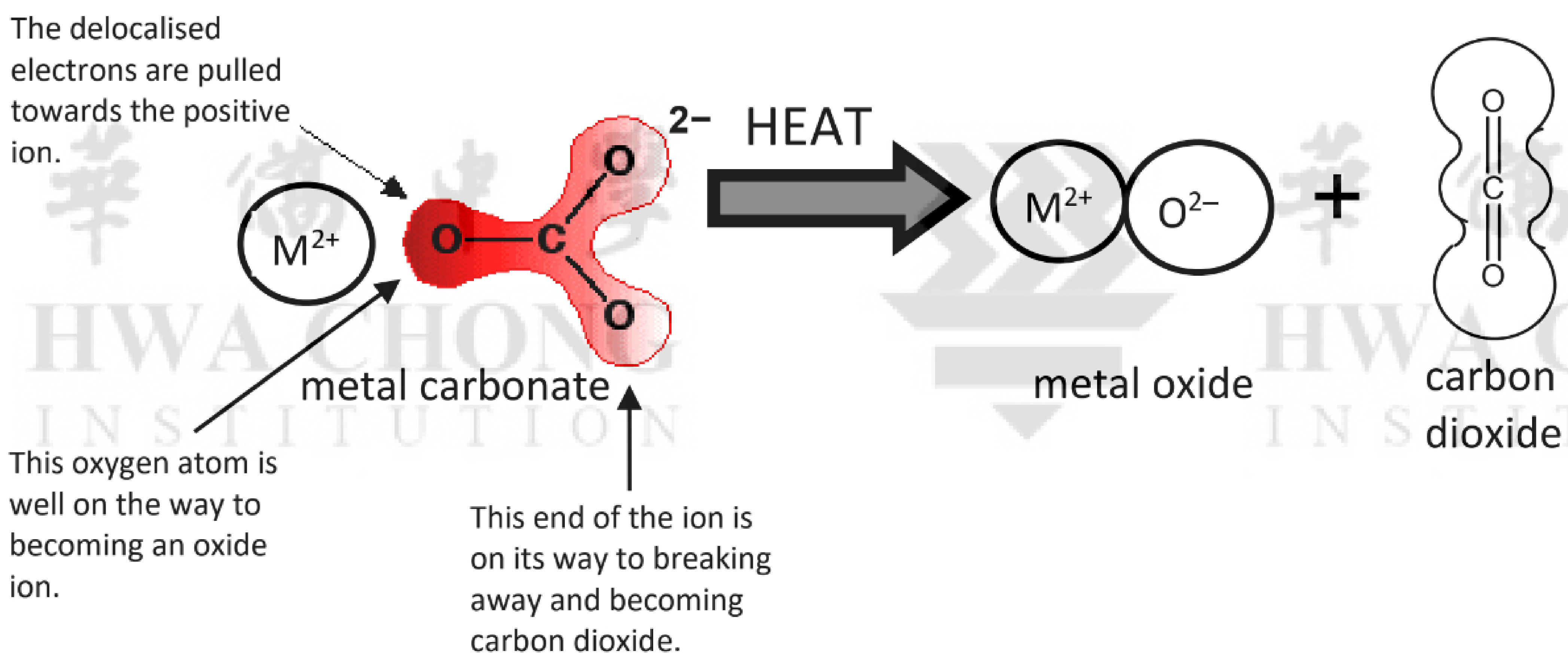
7.2.1 Factors affecting thermal stability

The thermal stability of the Group 2 carbonates is affected by the polarising power of the cation and the polarisability of the large anion.

- **Polarising power of the cation**

  Polarising power refers to the ability of a cation to distort the electron cloud of another ion, atom or molecule. In general, the higher the **<u>charge density of the cation</u>**, the greater the polarising power of the cation and the lower the thermal stability.

  The small and highly charged M^{2+} cation in these Group 2 compounds polarises the anion's larger electron cloud, weakening the covalent bonds within the anion. Hence these compounds decompose on heating as the weakened covalent bonds within the anion are easily broken.



The delocalised electrons are pulled towards the positive ion.

This oxygen atom is well on the way to becoming an oxide ion.

This end of the ion is on its way to breaking away and becoming carbon dioxide.

For Group 2 carbonates,

- **Cationic radius increases** down the group while charge remains the same
- Therefore **charge density of cation decreases** down the group
- **Polarising power of the cation decreases** down the group and is **less able to distort the electron cloud of the carbonate**, weakening the C–O bonds within the carbonate anion to a smaller extent
- **Covalent bonds** within the carbonate anion are **less likely to be broken** down the group
- The **ease of decomposition decreases** (or thermal stability increases) down the group so **higher temperature** is required to decompose the compound

- **Polarisability of large anion**

  Polarisability refers to the ease with which an anion, atom or molecule's electron cloud can be distorted by another. The greater the polarisability of the anion, the lower the thermal stability.

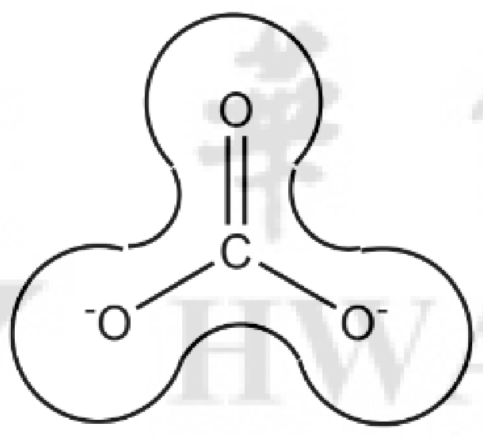
  - **Larger anions** are more susceptible to polarisation of their electron cloud.
  - Only **polyatomic anions** are susceptible to decomposition as monoatomic anions (e.g. O^{2-}, Cl^{-}) cannot be broken down further.

For your information

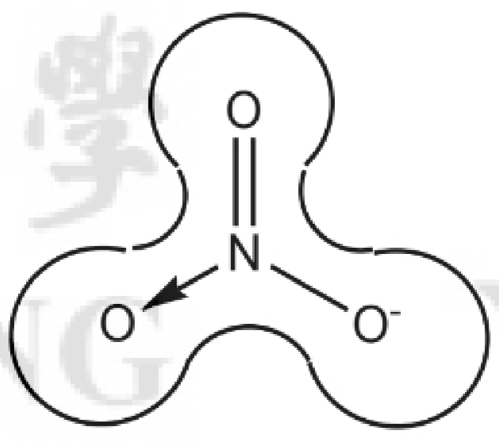
Other group 2 compounds that are susceptible to decomposition include nitrates and hydroxides, as these also have polarisable polyatomic anions and are thus also **unstable** towards heat.

Nitrates : $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + ½O_2(g)$

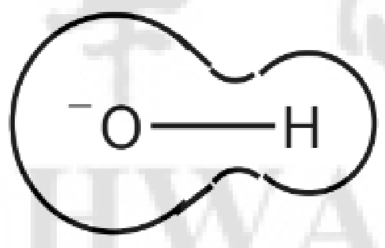
Hydroxides : $M(OH)_2(s) \rightarrow MO(s) + H_2O(g)$



carbonates

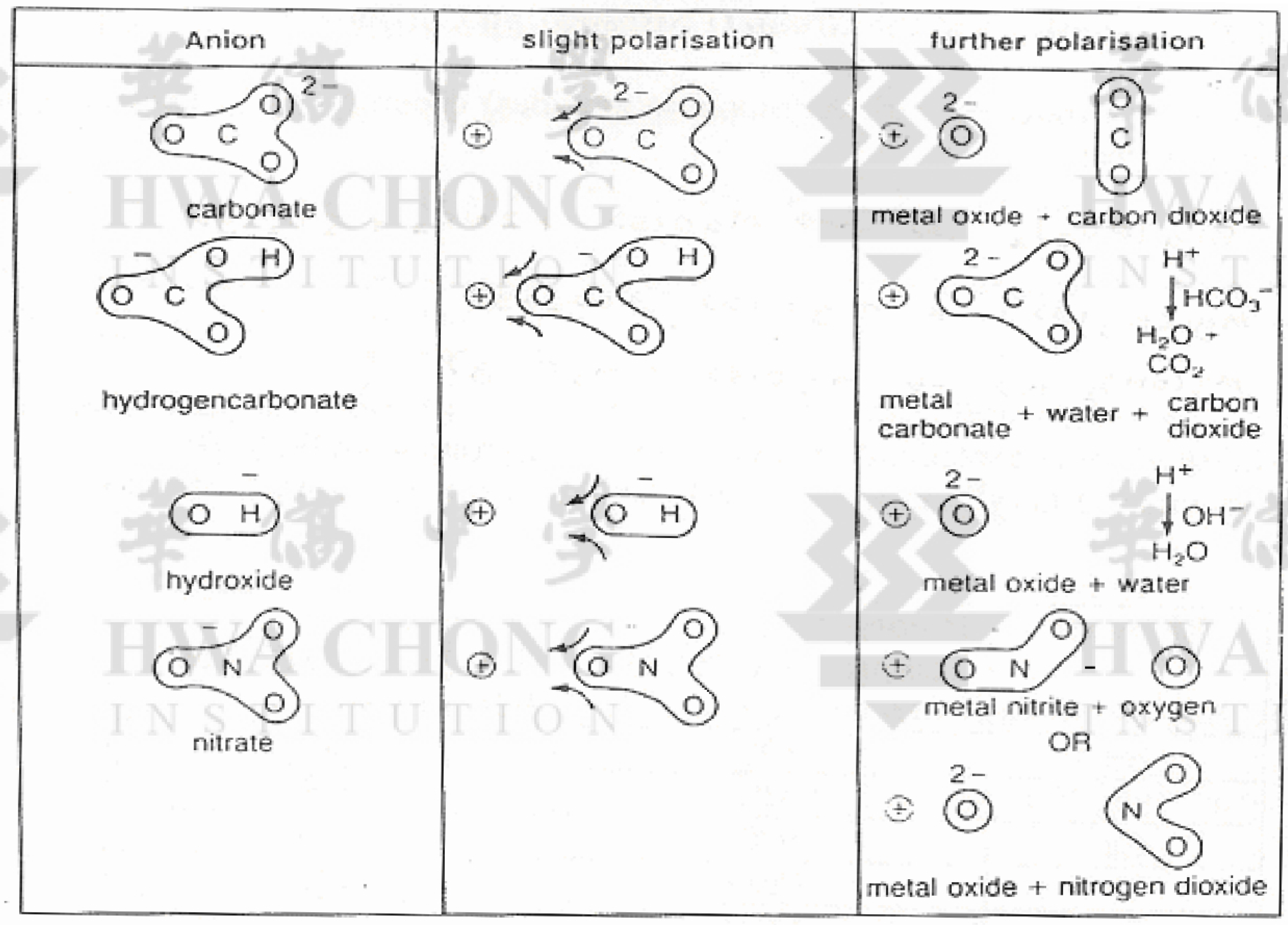


nitrates



hydroxides

The following table shows the products of decomposition of other polyatomic anions.



There are also other factors that may contribute to ease of decomposition of these compounds. One factor is the way the ions are packed in the lattice structure, as well as the ratio of cations to anions in the solid structure.

Lecture Exercise 7.1

1. Which of the following is the correct trend for Group 2 elements from Mg to Ba?

   A The reducing power decreases.
   B The elements become more electronegative.
   C The calcium cation has the highest charge density.
   D The decomposition temperature of the carbonates increases.

2. Which of the following statements concerning Group 2 elements, magnesium, calcium and barium are correct?

   1 Their reactivity increases with increasing atomic mass.
   2 The only oxidation state exhibited in their stable compounds is +2.
   3 On strong heating, the carbonates are stable to decomposition.

7.2.2 Comparison with thermal stability of Group 1 carbonates

The Group 1 carbonates are resistant to decomposition except for Li_2CO_3. The charge density of Li^+ is high enough to distort the carbonate's electron cloud so that the compound decomposes on heating.

$$\boxed{Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)}$$

The other Group 1 metal cations have low charge density due to their larger radii and so are unable to sufficiently distort the carbonate's electron cloud. Therefore the carbonates after lithium do not decompose on heating.

8 GROUP 17

8.1 Trend in volatility of Group 17 elements

LO 5(d): describe and explain the trend in volatility of the group 17 elements in terms of instantaneous dipole-induced dipole attraction

Table 5. Physical states, melting and boiling points of halogens

Element	No. of electrons	Melting point/ °C	Boiling point/ °C	Physical state at 20 °C
F_2	18	−220	−188	Gas
Cl_2	34	−101	−35	Gas
Br_2	70	−7	59	Liquid
I_2	106	114	184	Solid

The following table on the colour of halogens can be found in the *Data Booklet*:

Halogen	Colour of element	Colour in aqueous solution	Colour in hexane
Chlorine, Cl_2	Greenish yellow gas	Pale yellow	Pale yellow
Bromine, Br_2	Reddish brown gas/liquid	Orange	Orange-red
Iodine, I_2	Black solid/purple gas	Brown	Purple

The Group 17 elements, also known as the halogens, exist as simple, **non-polar diatomic** molecules with **dispersion forces** existing between molecules.

Down the group, the size of the electron cloud and hence, the polarisability of the halogen molecule increases. More energy is needed to overcome the stronger dispersion forces between the molecules. Hence, the **volatility of the halogens decreases** down Group 17, and the melting and boiling points **increase** down the group.

The increase in strength of dispersion forces down the group explains the change in physical state of the elements down Group 17.

8.2 Relative strength of Group 17 elements as oxidising agents

LO 5(f)(ii): describe and deduce from $E^\ominus$ values the relative reactivity of elements of Group 17 as oxidising agents

The outermost electron shell of halogens contains 7 electrons, i.e. ns^2 np^5. As such, their chemistry is dominated by a tendency to gain a completely filled outermost electron shell. Hence, halogens tend to be **reduced** in a redox reaction, and their oxidising power can be measured by the value of the standard reduction potential $E^\ominus$ for the process:

$$X_2(std) + 2e^- \rightleftharpoons 2X^-(aq)$$

The $E^\ominus$ values become less positive down the group, as shown in Table 6. Hence, the **oxidising power** of the halogens **decreases** down the group and they become less likely to be reduced in a redox reaction.

Table 6. Standard reduction potentials of the halogens

Element	F_2	Cl_2	Br_2	I_2
$E^\ominus$/ V	+2.87	+1.36	+1.07	+0.54

8.3 Redox reactions of Group 17 elements

LO 5(f)(ii): describe and deduce from $E^\ominus$ values the relative reactivity of elements of Group 17 as oxidising agents

This section describes some of the redox reactions that Group 17 elements undergo. In each of these reactions, the relative oxidising abilities of the halogens are further emphasised.

8.3.1 Displacement reactions

In general, a halogen higher in the group can oxidise a halide **below** it. A more reactive halogen will hence displace a less reactive one from its compounds.

Lecture Exercise 8.1

What observation would be made for the following? Explain your answer with the aid of chemical equations, where appropriate.

(a) Aqueous chlorine is added to a solution of KI.

(b) Potassium bromide solution is added to hexane (colourless liquid with a density of 0.659 g/cm^3 at 25 °C) in a test tube. Chlorine is bubbled through the potassium bromide layer.

8.3.2 Reactions with aqueous solutions containing iron(II) ions

In the presence of a halogen oxidising agent, an aqueous solution of Fe^{2+} ions can be oxidised to Fe^{3+}.

Lecture Exercise 8.2

By calculating the $E^\ominus_{cell}$ for the reaction between Fe^{2+} and the halogen, show that only chlorine and bromine are able to oxidise Fe^{2+} while iodine will not oxidise Fe^{2+}. (Given $E^\ominus(Fe^{3+}/Fe^{2+})$ = +0.77V)

Equation	$E^\ominus_{cell}$
$Cl_2(aq) + Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$	
$Br_2(aq) + Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$	
$I_2(aq) + 2Fe^{2+}(aq) \rightarrow 2I^-(aq) + 2Fe^{3+}(aq)$	

8.3.3 Reactions with thiosulfate, $S_2O_3^{2-}$

The decrease in oxidising power of the halogens can also be illustrated by their reaction with an aqueous solution of thiosulfate.

Chlorine and bromine would oxidise thiosulfate to sulfate, SO_4^{2-} while iodine oxidises thiosulfate to tetrathionate, $S_4O_6^{2-}$.

$$4Cl_2(aq) + \underset{+2}{S_2O_3^{2-}}(aq) + 5H_2O(l) \rightarrow 8Cl^-(aq) + \underset{+6}{2SO_4^{2-}}(aq) + 10H^+(aq)$$

$$4Br_2(aq) + \underset{+2}{S_2O_3^{2-}}(aq) + 5H_2O(l) \rightarrow 8Br^-(aq) + \underset{+6}{2SO_4^{2-}}(aq) + 10H^+(aq)$$

$$I_2(aq) + \underset{+2}{2S_2O_3^{2-}}(aq) \rightarrow 2I^-(aq) + \underset{+2.5}{2S_4O_6^{2-}}(aq)$$

Iodine is a weaker oxidising agent than chlorine and bromine, and hence the oxidation number of sulfur only increases from +2 to +2.5, as compared to from +2 to +6 in the reactions with chlorine or bromine.

8.4 Thermal stability of Group 17 hydrides

LO 5(g)(i): describe and explain the trend in thermal stability of Group 17 hydrides in terms of bond energies

Upon heating, the Group 17 hydrides (also called "hydrogen halides"), HX, can decompose to give hydrogen and the corresponding halogen.

$$2HX(g) \rightarrow H_2(g) + X_2(g)$$

The thermal stability of the hydrogen halide depends on the **strength of the H–X bond**.

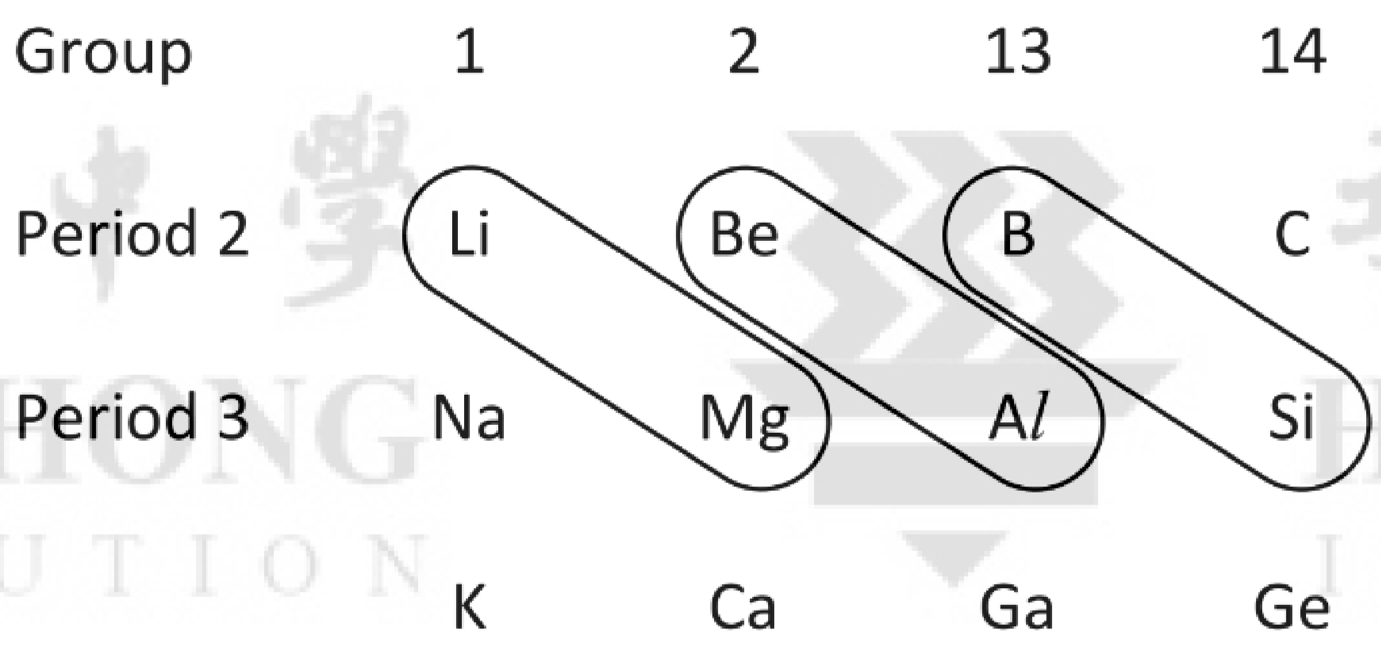
Table 7. Relationship between decomposition behaviour and H–X bond energy

Compound	HF	HCl	HBr	HI
Decomposition behaviour	Does not decompose even on strong heating	Does not decompose even on strong heating	Strong heating yields brown fumes of Br_2	Violet fumes of I_2 obtained when red-hot rod is plunged into jar of HI
H–X bond energy/ kJ mol^{-1}	562	431	366	299

- Down the group, as atomic radius increases from F to I, the bond length of the H–X bond increases and thus bond strength decreases.
- Hence, less energy is needed to break the H–X bond. Thus, the thermal stability of the hydrogen halides **decreases** down the group.

9 DIAGONAL RELATIONSHIPS IN THE PERIODIC TABLE

In the periodic table, certain pairs of diagonally adjacent elements in Period 2 and Period 3 (shown below) show similarities in their properties. They are said to have a diagonal relationship. As a result, the first element of some groups can be seen to have slightly different properties to the rest of the group.



Group	1	2	13	14
Period 2	Li	Be	B	C
Period 3	Na	Mg	A*l*	Si
	K	Ca	Ga	Ge

Examples of diagonal relationships:

- Li is the only Group 1 element that can form a nitride salt; all Group 2 elements form nitrides; etc.
- BeO and Al_2O_3 are both amphoteric; aqueous solutions of Be^{2+} and Al^{3+} are both weakly acidic due to hydrolysis; etc.
- B and Si tend to form covalent compounds rather than forming cations; both B and Si are semiconductors; etc.

Explanation

As we move across the period and down the group, the properties tend to have **<u>opposite trends</u>**:

For example, moving across the period, atomic radius decreases, but down the group, atomic radius increases. Similarly, moving across the period, electronegativity increases, while down the group, it decreases.

- Thus, moving *simultaneously* across the period and down the group by one element results in the combined effects of the opposing trends "cancelling out".

Note that diagonal relationships become less noticeable as we move beyond the B/Si pair, or below Period 3.

Lecture Exercise 9.1

1 Which element is likely to have an electronegativity similar to that of aluminium?

A barium **B** beryllium **C** carbon **D** chlorine

For your information: Formation of Be complexes

Beryllium forms complexes while the rest of the Group 2 metals do not:

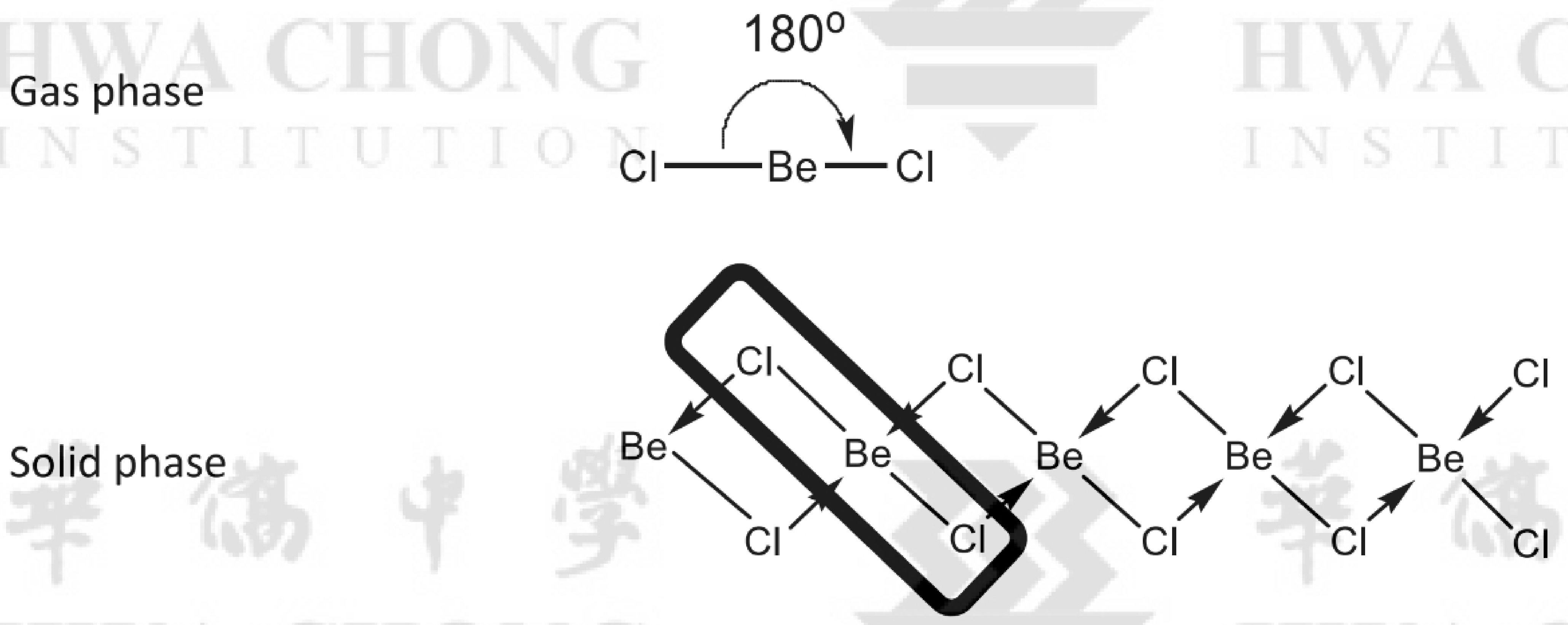
$$Be(OH)_2(aq) + 2OH^-(aq) \rightarrow [Be(OH)_4]^{2-}(aq)$$

$$BeF_2(s) + 2F^-(aq) \rightarrow [BeF_4]^{2-}(aq)$$

The reason for beryllium forming complexes lies in its electronic configuration. In binary compounds (e.g. $BeCl_2$), beryllium has only 4 valence electrons and has a coordination number of only 2. There is a tendency to achieve maximum coordination (and hence valence octet) by acting as a Lewis acid (electron pair acceptor) and forming a complex.

Beryllium has a maximum coordination number of 4 as it has only 4 available valence orbitals – one 2s & three 2p orbitals. There are no 2d orbitals and hence six-coordination is impossible.

This explains why in gaseous phase, $BeCl_2$ is a linear discrete molecule but in the solid state, $BeCl_2$ consists of linear polymers [compare it with $AlCl_3$ dimer].



LOOKING AHEAD

You have seen both physical and chemical trends of the elements and their compounds across Period 3. Moving on to the next topic on Transition Elements, it is helpful to bear in mind the properties of the metals in Group 1, 2 and 13 (e.g. Na, K, Mg, Ca, Al etc.) and to compare them to the properties of transition metals.