

St Andrew's Junior College H1 Chemistry 2021 Lecture Notes 6 The Periodic Table

## Assessment Objectives:

## Trends and variations in atomic and physical properties

For elements in the third period (sodium to chlorine), and in Group 17 (chlorine to iodine) candidates should be able to

- (a) recognise variation in the electronic configurations across a Period and down a Group
- (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
- (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)
- (d) describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction

## Trends and variations in chemical properties

For elements in the third period (sodium to chlorine) candidates should be able to

- (e) (i) state and explain the variation in the highest oxidation number of the elements in oxides (for Na<sub>2</sub>O; MgO; Al<sub>2</sub>O<sub>3</sub>; SiO<sub>2</sub>; P<sub>4</sub>O<sub>10</sub>; SO<sub>3</sub>) and chlorides (for NaC*l*; MgC*l*<sub>2</sub>; A*l*C*l*<sub>3</sub>; SiC*l*<sub>4</sub>; PC*l*<sub>5</sub>)
  (ii) state and explain the variation in bonding in oxides and chlorides in terms of electronegativity (with the exception of A*l*C*l*<sub>3</sub>)
  - (iii) describe the reactions of the oxides with water(for Na<sub>2</sub>O; MgO; Al<sub>2</sub>O<sub>3</sub>; SiO<sub>2</sub>; P<sub>4</sub>O<sub>10</sub>; SO<sub>3</sub>)

(iv) describe and explain the acid/base behaviour of oxides (for  $Na_2O$ ; MgO;  $Al_2O_3$ ; SiO<sub>2</sub>;  $P_4O_{10}$ ; SO<sub>3</sub>) and hydroxides (for NaOH; Mg(OH)<sub>2</sub>;  $Al(OH)_3$ ), 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<sub>2</sub>; AlCl<sub>3</sub>; SiCl<sub>4</sub>; PCl<sub>5</sub>)

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

For elements in Group 1 (lithium to caesium) and Group 17 (chlorine to iodine) candidates should be able to

- (f) describe and explain the relative reactivity of elements of:
  - (i) Group 1 as reducing agents in terms of ease of loss of electron;
  - (ii) Group 17 as oxidising agents in terms of ease of gain of electron
- (g) describe and explain the trend in thermal stability of Group 17 hydrides in terms of bond energies

In addition, candidates should be able to:

- (h) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity
- (i) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

# Content:

- 1. Introduction
- Variation of Atomic and Physical properties (Also see Atomic Structure & Chemical Bonding)
  - 2.1 Atomic Radius
  - 2.2 Ionic Radius
  - 2.3 First Ionisation Energy
  - 2.4 Electronegativity
  - 2.5 Melting Point
  - 2.6 Electrical Conductivity
- 3. Variation of Chemical Properties
  - 3.1 Oxidation number of Period 3 oxides and chlorides
  - 3.2 Period 3 oxides and their properties
    - 3.2.1 Bonding
    - 3.2.2 Reaction with water
    - 3.2.3 Acid-base nature of oxides and hydroxides
  - 3.3 Period 3 chlorides and their properties
    - 3.3.1 Bonding
    - 3.3.2 Reaction with water
  - 3.4 Group 1 elements
  - 3.5 Group 17
    - 3.5.1 Group 17 elements
    - 3.5.2 Group 17 hydrides
- 4. Application of concepts in Periodicity
  - 4.1 Predicting the characteristic properties of an element
  - 4.2 Diagonal relationship in the Periodic Table
  - 4.3 Deducing identity of unknown element from given information
- 5. Appendix

# **References:**

- Chemistry in Context by Graham Hill and John Holman
- Chemistry in Action by Michael Freemantle

Chemguide

http://www.chemguide.co.uk/inorganic/period3menu.html



### **1. INTRODUCTION**

(a) recognise variation in the electronic configurations across a Period and down a Group

Elements in the Periodic Table are arranged in **increasing order of proton number**. The modern Periodic Table is largely based on the works of Dmitri Mendeleev, Lothar Meyer and Henry Moseley. (See Appendix.)

#### The vertical columns are called groups.

Elements in the same group have the same number of valence electrons and outer electronic configuration. As such, they show similarities in their physical and chemical properties.

#### The horizontal rows are called periods.

Elements in the same period have the same number of filled quantum shells. They have different physical and chemical properties, but there are trends in these properties as we move across the period.

The elements are further grouped into four blocks in the periodic table.

- s-block [Groups 1 and 2]
- p-block [Groups 13 to 18]
- d-block [Transition metals] (JC2)
- f-block [Lanthanides & Actinides] (not in syllabus)

I         2         Group           1         2         1 <th>s–b</th> <th>lock</th> <th></th> <th>p-b</th> <th>lock</th> <th></th> <th></th>	s–b	lock													p-b	lock		
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#### 2. VARIATION OF ATOMIC AND PHYSICAL PROPERTIES

(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

## 2.1 Atomic Radius (refer to Atomic Structure lecture notes)



# Trend: Atomic radius decreases across the period.

Reason: Across a period,

- Nuclear charge increases as number of protons increase.
- Shielding effect is approximately constant as successive electrons are added to the same quantum shell
- Effective nuclear charge increases
- Valence electrons are more strongly attracted towards the nucleus

# Trend: Atomic radius increases down the group.

Reason: Down a group,

- Although nuclear charge increases as number of protons increase,
- the more significant factor is the increased number of filled quantum shells
- causing the valence electrons to be further away from the nucleus

#### 2.2 Ionic Radius (refer to Atomic Structure lecture notes)



#### Reason:

- Nuclear charge remains constant (as number of protons in both the atom and its cation are the same).
- The cation has **fewer electrons** than its atom, thus, the remaining electrons are more strongly attracted to the nucleus.
- Furthermore, the cation contains one less filled quantum shell.
- (b) Anionic radius is greater than corresponding parent atom

#### Reason:

• Nuclear charge remains constant (as number of protons in both the atom and its anion are the same).

r<sub>atom</sub> < r<sub>anion</sub>

• The anion has **more electrons than protons**, thus, the valence electrons are less strongly attracted to the nucleus.

#### (c) Ionic Radius of Isoelectronic Species

Trend: Ionic radius of isoelectronic ions decrease across the period.

There are 2 sets of isoelectronic ions.

Cations:	$Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$	[1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> ]
Anions:	$P^{3-} > S^{2-} > Cl^{-}$	[1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> ]

Reason:

- Nuclear charge increases as number of protons increase.
- Shielding effect is approximately constant as the ions are isoelectronic
- Effective nuclear charge increases
- Valence electrons are more strongly attracted to the nucleus.

There is a sharp increase in ionic radius from the cationic series (Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Si<sup>4+</sup>) to the anionic series (P<sup>3-</sup>, S<sup>2-</sup>, Cl), as these 2 series are **NOT** isoelectronic. The anions have **1 more filled quantum shell** than the cations, causing the valence electrons to be further away from the nucleus.

# 2.3 First ionisation energies (refer to Atomic Structure lecture notes)



# Trend: First ionisation energy generally increases across a period.

Reason: Across a period,

- Nuclear charge increases as number of protons increase
- Shielding effect is approximately constant as successive electrons are added to the same valence shell
- Effective nuclear charge increases
- Valence electrons are more strongly attracted to the nucleus
- More energy is required to remove a valence electron from each atom.

## (i) Irregularities at Group 2 and Group 13

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1^{st} IE of Al < 1^{st} IE of Mg
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 $_{12}$ Mg: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup>  $_{13}$ A/: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>1</sup>

- In Mg, the first electron is removed from the **3s** orbital. In A*l*, the first electron is removed from the **3p** orbital.
- The **3p** orbital is **further** away from the nucleus than the 3s orbital and **experiences additional shielding effect** by the two 3s electrons.
- These factors outweigh the effect of increase in nuclear charge from Mg to A*l*, resulting in a weaker attraction by nucleus
- Less energy is required to remove an electron from the 3p than the 3s orbital.

(A similar explanation can be applied to Boron & Beryllium in Period 2.)

## (ii) Irregularities at Group 15 and Group 16

### $1^{st}$ IE of S < $1^{st}$ IE of P



- In S, the electron to be removed is originally **paired** and experiences **inter-electronic repulsion** from 2 electrons occupying the same orbital.
- This factor outweighs the effect of increase in nuclear charge from P to S, resulting in a weaker attraction by nucleus.
- Less energy is required to remove the paired 3p electron in S compared to the unpaired 3p electron in P.

(A similar explanation can be applied to Oxygen & Nitrogen in Period 2.)

# Trend: First ionisation energy <u>decreases</u> down a group.

Reason: Down a group,

- Nuclear charge increases as number of protons increase.
- However, the more significant factor is the **increased number of filled quantum shells**
- causing the valence electrons to be further away from the nucleus.
- Valence electrons are less strongly attracted to the nucleus
- Less energy is required to remove the valence electron

## 2.4 Electronegativity (refer to Atomic Structure lecture notes)

The electronegativity of an atom refers to the ability of an atom in a molecule to **attract bonding electrons**.



# Trend: Electronegativity *increases* across a period.

Reason: Across a period,

- Nuclear charge increases as number of protons increase
- Shielding effect is approximately constant as successive electrons are added to the same valence shell
- Effective nuclear charge increases

Hence, the ability of the atom to attract bonding electrons increases-

Trend: Electronegativity <u>decreases</u> down a group.

Reason: Down a group,

- Nuclear charge increases as number of protons increase
- However, the more significant factor is the increased number of filled quantum shells
- causing the valence electrons to be further away from the nucleus.

Hence, the ability of the atom to attract bonding electrons decreases.

#### 2.5 Melting Point (refer to Chemical Bonding lecture notes)

(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)



# **Trend:** Melting point <u>increases</u> from sodium to silicon and then <u>decreases</u> from phosphorus to chlorine.

We explain the variation in melting points by considering the elements' **structure**, **bonding and particles**. Always link the melting point to the **energy** required to overcome the attractions between the particles.

## Na, Mg and Al

Na, Mg and A*l* have a **giant metallic lattice** of **cations surrounded by a sea of delocalised electrons**, held together by **strong metallic bonds**. A large amount of energy is required to overcome the strong metallic bonds, hence, high melting point.

The melting point increases from Na to Al as metallic bond strength increases with

- increasing number of valence electrons
- increasing charge
- decreasing cationic size

# Si

Si has a **giant molecular structure** consisting of **atoms** held together by **strong covalent bonds**. A large amount of energy is required to break the many strong covalent bonds, thus, melting point is very high.

# P<sub>4</sub>, S<sub>8</sub> and Cl<sub>2</sub>

 $P_4$ ,  $S_8$  and  $Cl_2$  have simple molecular structures with weak instantaneous dipole – induced dipole attractions between molecules. Little energy is required to overcome these weak attractions, hence low melting point.

The melting point of  $S_8 > P_4 > Cl_2$ .  $S_8$  has the largest number of electrons per molecule, followed by  $P_4$  then  $Cl_2$ . The larger the number of electrons per molecule, the more polarisable the electron cloud and the stronger the instantaneous dipole – induced dipole attraction between molecules.

2.6 Electrical Conductivity (refer to Chemical Bonding lecture notes)



**Trend:** Electrical conductivity increases from Na to A*l*, drops sharply from A*l* to Si, decreases to 0 from P to C*l*.

Electrical conductivity depends on the presence of **mobile charge carriers** (mobile ions or electrons).

## <u>Na, Mg and Al</u>

The metals have delocalised electrons to act as mobile charge carriers. From Na to A*l*, number of **delocalised electrons** increases from 1 to 3, therefore there is an increase in electrical conductivity of these metals.

# Si

Si is a semi-conductor/metalloid (has properties of metals and non metals). It has a low electrical conductivity.

More on semiconductors: <u>https://www.youtube.com/watch?v=wuLuBroXAKo</u> (not in syllabus)

# P<sub>4</sub>, S<sub>8</sub> and Cl<sub>2</sub>

 $P_4$ ,  $S_8$ ,  $C_{l_2}$  are simple molecules with **no delocalised electrons** to act as mobile charge carriers. The valence electrons are localised in chemical bonds.



Self- Check: Q1-2

# 3. VARIATION OF CHEMICAL PROPERTIES

#### 3.1 Oxidation Numbers of Period 3 oxides and chlorides

(e)(i) state and explain the variation in the highest oxidation number of the elements in oxides (for Na<sub>2</sub>O; MgO;  $A_{l_2}O_3$ ; SiO<sub>2</sub>; P<sub>4</sub>O<sub>10</sub>; SO<sub>3</sub>) and and chlorides (for NaCl; MgCl<sub>2</sub>; AlCl<sub>3</sub>; SiCl<sub>4</sub>; PCl<sub>5</sub>)

Element	Na	Mg	Al	Si	Р	S
Formula of oxide	Na <sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	$P_4O_{6,} P_4O_{10}$	SO <sub>2,</sub> SO <sub>3</sub>
Oxidation number	+1	+2	+3	+4	+3, +5	+4, +6

Element	Na	Mg	Al	Si	Р	
Formula of chloride	NaC <i>l</i>	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>	PCl <sub>3</sub> , PCl <sub>5</sub>	
Oxidation number	+1	+2	+3	+4	+3, +5	

The oxidation number of each element in its oxide and chloride is always **positive** because O and Cl are more electronegative than the element.

The highest oxidation number of each element corresponds to the number of valence electron(s) in each atom of the element that can be lost or shared to achieve an octet configuration of ns<sup>2</sup> np<sup>6</sup>.

P and S can exhibit variable oxidation states. They are able to expand their octet structure due to the presence of **empty and energetically accessible 3d orbitals**.

## 3.2 Period 3 oxides and their properties

#### 3.2.1 Bonding

(e)(ii) state and explain the variation in bonding in oxides in terms of electronegativity
 (e)(iv) suggest the types of structure and bonding present in the oxides from observations of their chemical and physical properties

# Trend: Across Period 3, the oxides become less ionic and more covalent.

Reason:

- The elements change from metallic to non-metallic across the period.
- Electronegativity difference between the element and oxygen decreases, resulting in more covalent character.

Formula of oxide and state at rtp	Na₂O(s)	MgO(s)	A/2O3(s)	SiO₂(s)	P <sub>4</sub> O <sub>10</sub> (s)	SO₃( <i>l</i> )	
Bonding		lonic		Covalent			
Structure	Giant ionic lattice structure Large amount of energy required to overcome strong attractive forces between oppositely charged ions → High mp			Giant molecular structureSimple molecular structureLarge amount of energy required to overcomeSmall amount of energy required to overcome weak instantaneous dipole – induced dipole forces of attraction between molecules → Low mp			
Melting point trend		Melting Point	Na <sub>2</sub> O MgO /	A/2O3 SiO2 I	P4O10 SO3		
Electrical conductivity	In solid state: <b>non conducting</b> In molten state: <b>good conductor</b> – mobile ions act as mobile charge carriers			In all states: <b>non conducting</b> No mobile ions or electrons to act as mobile charge carriers			

#### 3.2.2 Reaction with water

(e)(iii) describe the reactions of the oxides with water(for Na<sub>2</sub>O; MgO; Al<sub>2</sub>O<sub>3</sub>; SiO<sub>2</sub>;P<sub>4</sub>O<sub>10</sub>; SO<sub>3</sub>)
(e)(vi) suggest the types of structure and bonding present in the oxides from observations of their chemical and physical properties

# **Trend**: Across Period 3, the nature of the oxides changes from basic to amphoteric to acidic (become more acidic).

	Reaction with water	Equations	рН
Na₂O	Reacts vigorously and exothermically to form a colourless, <b>strongly alkaline</b> solution.	Na <sub>2</sub> O(s) + H <sub>2</sub> O( <i>l</i> ) → 2NaOH(aq)	13
MgO	Very slow reaction. MgO is only slightly soluble in water. (Appears to be insoluble.) Reacts less readily (due to its more exothermic lattice energy) to form a <b>weakly</b> <b>alkaline</b> solution.	$MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$	9
Al <sub>2</sub> O <sub>3</sub>	<b>Does not react</b> with water due to its highly exothermic lattice energy. Al <sub>2</sub> O <sub>3</sub> is insoluble in water.	NA	7
SiO <sub>2</sub>	<b>Does not react</b> with water due to the strong covalent bonds between Si and O atoms in the giant covalent lattice structure. SiO <sub>2</sub> is insoluble in water.	NA	7
P <sub>4</sub> O <sub>10</sub>	Reacts vigorously to form a colourless, <b>acidic</b> solution.	$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$	2
SO₃	Reacts vigorously and exothermically to form a colourless, <b>strongly acidic</b> solution.	$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$	2
pH trend	pH of resultant mixture	SiO <sub>2</sub> P <sub>4</sub> O <sub>10</sub> SO <sub>3</sub> –	

#### 3.2.3 Acid-Base nature of oxides and hydroxides

(e)(iv) describe and explain the acid/base behaviour of oxides (for Na<sub>2</sub>O; MgO; Al<sub>2</sub>O<sub>3</sub>; SiO<sub>2</sub>; P<sub>4</sub>O<sub>10</sub>; SO<sub>3</sub>) and hydroxides (for NaOH; Mg(OH)<sub>2</sub>; Al(OH)<sub>3</sub>), including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids.

# **Trend**: Across Period 3, the nature of the oxides changes from basic to amphoteric to acidic.

Oxide	Na <sub>2</sub> O	MgO	A <i>I</i> <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub>	SO <sub>3</sub>
Hydroxide	NaOH	Mg(OH)₂	Al(OH)₃	NA		
Nature of oxide (and hydroxide if applicable)	Ba React vigorous form salt	<b>sic</b> Ily with acids to and water	Amphoteric React with both acids and bases to form salt and water	React with	Acidic alkalis to form sal	It and water

 $Al_2O_3$  is an ionic oxide.  $Al^{3+}$  has high charge density and hence, high polarising power, and is able to polarise the small  $O^{2-}$  ion, giving  $Al_2O_3$  some covalent character. The mixture of ionic and covalent character causes  $Al_2O_3$  to display both basic and acidic properties – making it amphoteric.

	Reaction with HCl	Reaction with NaOH
Na₂O	$Na_2O(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l)$	
NaOH	$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$	NA
MgO	$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$	
Mg(OH)₂	$Mg(OH)_2(aq) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$	
Al <sub>2</sub> O <sub>3</sub>	$Al_2O_3(s)$ + 6HCl(aq) → 2AlCl <sub>3</sub> (aq) + 3H <sub>2</sub> O(l)	$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4]$ (aq) sodium aluminate
A/(OH)₃	$A_l(OH)_3(s) + 3HC_l(aq) \rightarrow A_lC_l_3(aq) + 3H_2O(l)$	A/(OH)₃(s) + NaOH(aq) → Na[A/(OH)₄](aq)
SiO₂	NA	Does not react with NaOH under laboratory conditions. Reacts with only with <b>hot</b> , <b>concentrated</b> alkalis to form silicates. SiO <sub>2</sub> (s) + 2NaOH(conc) → Na <sub>2</sub> SiO <sub>3</sub> (aq) + H <sub>2</sub> O( <i>l</i> )
P <sub>4</sub> O <sub>10</sub>		$P_4O_{10}(s)$ + 12NaOH(aq) → 4Na <sub>3</sub> PO <sub>4</sub> (aq) + 6H <sub>2</sub> O( $l$ )
SO <sub>3</sub>		$SO_3(l) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$



## 3.3 Period 3 chlorides and their properties

#### 3.3.1 Bonding

Candidates should be able to:

(e)(ii) state and explain the variation in bonding in chlorides in terms of electronegativity (with the exception of  $A/Cl_3$ )

(e)(vi) suggest the types of structure and bonding present in the chlorides from observations of their chemical and physical properties.

# Trend: Across Period 3, the chlorides become less ionic and more covalent.

Reason:

2

- The elements change from metallic to non-metallic across the period.
- Electronegativity difference between the element and chlorine decreases, resulting in more covalent character.

Formula of chloride and state at rtp	NaCl(s) MgCl <sub>2</sub> (s)		A/Cl₃(s)	SiCl₄(l)	PCl₅(s)		
Bonding		lonic	<b>Covalent</b> *High charge density of Al <sup>3+</sup> polarises the large electron cloud of Cl <sup>-</sup> ion, hence making the bonding in AlCl <sub>3</sub> covalent.				
	Giant ioni	c lattice structure	Simple molecular structure				
Structure	Large amour overcome s between opp	nt of energy required to trong attractive forces ositely charged ions → High mp	Small amount of energy required to overcome weak instantaneous dipole – induced dipole forces of attraction between molecules → Low mp				
Melting point trend		Melting point	MgCl <sub>2</sub> AlCl <sub>3</sub> SiCl <sub>4</sub>	PCIs			
Electrical conductivity	In so cc In molt	lid state: <b>non</b> onducting en state: <b>good</b>	In all st No mobile ions	ates: <b>non c</b> s or electror	onducting ns to act as mobile		
	<b>conductor</b> – mobile ions act as mobile charge carriers						

## 3.3.2 Reaction with water

Candidates should be able to:

(e)(v) describe and explain the reactions of the chlorides with water (for NaCl; MgCl<sub>2</sub>; AlCl<sub>3</sub>; SiCl<sub>4</sub>; PCl<sub>5</sub>)

	Reaction with water	Equations	рН
NaCl	Dissolves in water to form a colourless, <b><u>neutral</u></b> solution.	$NaCl(s) + aq \rightarrow Na^{+}(aq) + Cl^{-}(aq)$	7
	Na <sup>+</sup> and Cl <sup>-</sup> form ion-dipole interactions with water molecules.		
	Na <sup>+</sup> (and C <i>l</i> <sup>-</sup> ) has low charge density and does not undergo hydrolysis (reaction with water molecules).	5+ H 5+ CI-mm Zx	

	Reaction with water	Equations	рН
MgCl <sub>2</sub>	Dissolves in water to form a colourless, <b>slightly acidic solution</b> . Mg <sup>2+</sup> has a higher charge density than Na <sup>+</sup> and undergoes <b>partial</b> <b>hydrolysis</b> (reversible arrow) in water. The high charge density of Mg <sup>2+</sup> polarises the electron cloud of water, weakening the O–H bond, releasing a small amount of H <sup>+</sup> ions and causing the solution to be slightly acidic.	Hydration: MgCl <sub>2</sub> (s) + 6H <sub>2</sub> O(l) → $[Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$ Partial hydrolysis: $[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \Rightarrow$ $[Mg(OH)(H_2O)_5]^{+}(aq) + H_3O^{+}(aq)$	6.5
A/Cl <sub>3</sub>	<ul> <li>1. Large amount of water <ul> <li>(i.e. adding A/Cl<sub>3</sub> to an excess of water)</li> </ul> </li> <li>Dissolves in water to form a colourless, <u>acidic solution</u>.</li> <li>Al<sup>3+</sup> has a higher charge density than Mg<sup>2+</sup> and undergoes a larger extent of <u>hydrolysis</u> in water (but still partial hydrolysis), releasing more H<sup>+</sup> ions and causing the solution to be more acidic.</li> </ul>	1. Large amount of water Hydration: $A/Cl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ Partial hydrolysis: $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$ $\int_{A(H_2O)_6J^{3+}} + \bullet = \int_{H_2O} \int_{A(H_2O)_5OHJ^{2+}} + \bullet + \int_{H_5O^+} + \bullet + \int_{H_5O^+} + \bullet + \int_{H_5O^+} + \bullet + \int_{H_5O^+} + \int_{H_5$	3
	<ul> <li>2. Limited amount of water</li> <li>(i.e. adding a few drops of water to solid A/Cl<sub>3</sub>)</li> <li>Reacts violently to form white fumes of HCl and a white solid.</li> </ul>	2. Limited amount of water $A/Cl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$ white solid steamy white fume	S
SiCl <sub>4</sub>	Reacts vigorously with water. Undergoes <u>complete hydrolysis</u> (full arrow) in water to form a white solid and a colourless, <u>strongly</u> <u>acidic</u> solution. White fumes of HC <i>l</i> gas are seen (most HC <i>l</i> gas dissolves to form HC <i>l</i> (aq)). The solution is strongly acidic due to the hydrochloric acid produced.	SiC $l_4(l)$ + 2H <sub>2</sub> O( $l$ ) $\rightarrow$ SiO <sub>2</sub> (s) + 4HC $l$ (aq) Reaction of SiC $l_4$ with water <u>https://www.youtube.com/watch?v=Xhps2HDpTwl</u>	2

	Reaction with water	Equations	рН
	Complete hydrolysis can take place due to the presence of empty and energetically accessible 3d orbitals in Si which can be attacked by the lone pairs of electrons on the oxygen atom of water molecules.	$\begin{array}{c} H_{2}0: & H_{2}0: & H_{2}0: & H_{2}0 \\ C_{I} & S_{I} & C_{I} & C_{I} & S_{I}^{-} & C_{I} & C_{I} & S_{I}^{-} & C_{I} \\ C_{I} & S_{I} & C_{I} & C_{I} & S_{I}^{-} & C_{I} & C_{I} & C_{I} & C_{I} & C_{I} \\ \end{array}$ Note: For simplicity, only one lone pair of electrons is shown on the oxygen atom of the water molecule.	
PCl <sub>5</sub>	1. Large amount of water	1. Large amount of water	2
	Reacts vigorously with water. Undergoes <u>complete hydrolysis</u> (full arrow) in water to form a colourless, <u>strongly acidic</u> solution. White fumes of HC <i>I</i> gas are seen (most HC <i>I</i> gas dissolves to form HC <i>I</i> (aq)). The solution is strongly acidic due to the hydrochloric acid produced. Complete hydrolysis can take place due to the presence of empty and energetically accessible 3d orbitals in P which can be attacked by the lone pairs of electrons on the oxygen atom of water molecules.	PC <i>l</i> <sub>5</sub> (s) + 4H <sub>2</sub> O( <i>l</i> ) → H <sub>3</sub> PO <sub>4</sub> (aq) + 5HC <i>l</i> (aq)	
	2. Limited amount of water or cold	2. Limited amount of water	
	(i.e. PC <i>l</i> <sub>5</sub> : H <sub>2</sub> O = 1:1)	PC $l_5(s)$ + H <sub>2</sub> O( $l$ ) → POC $l_3(l)$ + 2HC $l(g)$ When more water is added: POC $l_3(l)$ + 3H <sub>2</sub> O( $l$ ) → H <sub>3</sub> PO <sub>4</sub> (aq) + 3HC $l$ (aq)	
pH trend	pH of resultant 7 NaC/	t mixture MgC/2 AiC/s SiC/s PC/s	

Exercise 3	<ul> <li>Thinking process:</li> <li>Which period does C and Si belong to?</li> </ul>
Why does SiCl <sub>4</sub> hydrolyse readily in water whereas CCl <sub>4</sub> is inert?	<ul> <li>Why is SiCl<sub>4</sub> able to react readily with water?</li> </ul>
Ans:	
• Si is in Period 3 and has <b>empty and energetically accessible 3d orl</b> lone pair of electrons on the oxygen atom of water molecules.	bitals which can be attacked by the

- C is in Period 2, it has **no empty and energetically accessible 3d orbitals** to accept electrons from water and hence, CCl<sub>4</sub> is inert in water (does not undergo hydrolysis).
- Furthermore, in CCl<sub>4</sub>, the four large chlorine atoms around C atom could hinder any approach of water molecules.



## 3.4 Group 1 elements

(f) (i) describe and explain the relative reactivity of elements of Group 1 as reducing agents in terms of ease of loss of electron

## Reactivity of Group 1 Elements (Li to Cs)

- Group 1 elements are <u>reactive</u> metals.
  - Li, Na, K, Rb and Cs are very reactive and therefore they are stored in oil.
- Group 1 elements generally act as **reducing agents and undergo oxidation** to the <u>+ 1</u> oxidation state in all their compounds by losing the outermost electron so as to achieve stable configuration of noble gases.

 $M \rightarrow M^+ + e^-$ 

Hence, most of the Group 1 compounds are *ionic* in nature.

Element	Atomic radius/nm	tomic radius/nm 1 <sup>st</sup> ionisation energy	
		$M(g) \rightarrow M^{+}(g) + e^{-}$	
Li	0.152	519	
Na	0.186	495	
К	0.190	418	
Rb	0.265	403	
Cs	0.298	376	

 Reducing powers (and hence reactivity) <u>increases</u> down the group because atomic radius increases and 1<sup>st</sup> ionisation energies decreases. Down the group, atoms are more willing to give up their valence electron to form cation, M<sup>+</sup>.

∽ Self- Check: Q7

## 3.4 Group 17 elements

- (d) describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction
- (f) (ii) describe and explain the relative reactivity of elements of Group 17 as oxidising agents in terms of ease of gain of electron

#### (a) Structure and Properties

- Group 17 elements (also called <u>halogens</u>) are p-block elements with a characteristic outer-shell configuration of <u>ns<sup>2</sup> np<sup>5</sup></u>.
- Halogens have seven electrons in the outermost shell and will complete the octet by accepting an electron to form a halide, X<sup>-</sup>, or by sharing an electron to form a covalent bond. Halogen elements exist as diatomic molecules, X<sub>2</sub>.

Element	Fluorine (F)	Chlorine (Cl)	Bromine (Br)	lodine (I)
Outer electronic				
configuration	2s² 2p⁵	3s² 3p⁵	4s² 4p <sup>5</sup>	5s² 5p <sup>5</sup>
Physical state at 25°C	Gas	Gas	Liquid	Solid
Colour	Pale yellow	Greenish	Reddish-	Black
		yellow	brown	
Melting point / °C	-220	-101	-7	113
Boiling point / °C	-188	-34	59	184
Solubility in water	-	Moderately	Slightly	Insoluble
		soluble	soluble	
Solubility in organic	-	Pale yellow	Orange red	Violet/
solvent		solution	solution	purple solution
1st Electron affinity/	-332*	-349	-325	-295
kJ mol⁻¹				
Bond energy / (X-X)	158*	244	193	151
kJ mol⁻¹				

#### (b) Volatility of Halogen

(d) describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction.

	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
Boiling point / °C	-188	-35	59	183

Trend: Volatility decreases down Group 17.

**Reason:** Halogens exist as non-polar simple covalent molecules with weak instantaneous dipole-induced dipole (id-id) interactions between its molecules.

Down the group

- number of electrons per molecule increases
- the electron cloud size of X<sub>2</sub> increases
- electron cloud becomes more easily distorted/ polarisable
- instantaneous dipole-induced dipole attraction become stronger.
- more energy is required to break the intermolecular forces of attraction
- hence, **boiling point** increases in the order: F<sub>2</sub> < Cl<sub>2</sub> < Br<sub>2</sub> < I<sub>2</sub>
- volatility <u>decreases</u> in the order:  $F_2 > Cl_2 > Br_2 > I_2$



Ans: 1,2,3

## (c) Reactivity of Group 17 Elements

• Halogens are **oxidising agents**. (The more likely a halogen is reduced, the stronger its oxidising power.)

# Trend: Oxidising power of X<sub>2</sub> decreases down Group 17

#### Reason:

**Oxidising powers** (and hence reactivity) <u>decreases</u> down the group because **atomic radius increases** and **electron affinity decreases**. Down the group, atoms have **less tendency to gain electron** to form anion, X<sup>-</sup>.

#### (c) Reactions to illustrate the relative oxidising power of the halogens

#### 1. Displacement reactions

• A more reactive/ oxidising halogen will displace a less reactive/oxidising halogen from its compound.

	Halide			
Halogen	chloride, C <i>l</i> ⁻	bromide, Br⁻	iodide, I⁻	
Chlorine, Cl <sub>2</sub>		Chlorine <b>can displace</b> bromine from aq solution of bromide $Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$ <b>Observations:</b> Br <sub>2</sub> , Orange in aq. solution / orange -red if dissolved in CCl <sub>4</sub>	Chlorine <b>can displace</b> iodine from aq solution of iodide $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$ <b>Observations:</b> $I_2$ , Brown in aq. solution / Purple if dissolved in CCl <sub>4</sub>	
Bromine, Br <sub>2</sub>	No reaction		Bromine <b>can displace</b> iodine from aq. solution of iodide; $Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$ <u><b>Observations:</b></u> $I_2$ , Brown in aq. solution / Purple if dissolved in CC $l_4$	
lodine, $I_2$	No reaction	No reaction		



# Watch Video: Displacement reaction of halogens

## https://www.youtube.com/watch?v=rBhMWpyO7Ts

View the colour change when a more reactive halogen displace a less reactive halogen from its compound.



Watch Video: Group 7 Halogens https://www.youtube.com/watch?v=yW\_C10cEzMk

Understand halogens and view its displacement reaction, reaction with metals and reaction with hydrogen.

# 3.5 Group 17 hydrides (Hydrogen halides, HX)

# (a) Formation of Group 17 hydrides (Hydrogen halides)

• Halogens, in the gaseous state, react with gaseous hydrogen to produce hydrogen halides  $X_2(g) + H_2(g) \rightarrow 2HX(g) X = F, Cl, Br$ 

# (b) Thermal stability of Group 17 halides

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

	H – F	H – C <i>l</i>	H – Br	H – I
Bond energy	+562	+431	+366	+299
/ kJ mol⁻¹				
Decomposition	-	-	2HBr(g)	2HI (g) 🗲
Reaction			$H_2(g) + Br_2(g)$	$H_2(g) + I_2(g)$
			reddish brown	Purple fumes
			vapour observed	observed
Comment	stable	stable to	decomposed	easily decomposed
	to heat	heat	slightly when	when heated
			heated.	

# Trend: Thermal stability of Group 17 hydrides decreases down the group

#### Reason:

- Thermal stability of Group 17 hydrides is related to the H-X bond strength
- More endothermic bond energy suggests that the H-X bond is stronger and that H-X is more thermally stable.
- Down the group, the size of the halogen increases.
- The valence orbital used for bonding is larger and more diffuse.
- Less effective orbital overlap between s orbital of hydrogen and the valence p orbital of the halogen.
- Electronegativity difference between hydrogen and halogen decreases, resulting in a decrease in bond polarity.
- Hence H X bond strength decreases, so H X bond is more easily broken.
- Hence the thermal stability of the hydrogen halides decreases down the group

#### ∽ Self- Check: 8-10

Exercise 6
For the sequence hydrogen chloride, hydrogen bromide and hydrogen iodide, there
is an increase in
<ol> <li>Thermal stability</li> <li>Bond length</li> <li>Volatility</li> </ol>
Ans: 2

# 4. APPLICATION OF CONCEPTS IN PERIODICITY

- (h) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity
- (i) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

## 4.1 Predicting the characteristic properties of an element

- Elements in the same Group tend to have similar chemical and physical properties.
- You can use knowledge of the Period 3 elements to extrapolate the chemical and physical behaviour of other elements in Groups 1-2, 12-17.



# Exercise 7

The element selenium can react with oxygen to form several compounds. From your knowledge of chemical periodicity, suggest the chemical formulae of two of the compounds selenium forms with oxygen.

Thinking process:
Which elements are in the same Group as selenium?

formula?

What oxides do these elements form, and what is their

Ans: SeO<sub>2</sub>, SeO<sub>3</sub>

# 4.2 Diagonal Relationship in the Periodic Table

 It was observed that for certain properties, the trends actually move in opposite directions. For example, electronegativity increases across a Period but decreases down a Group. When taken into combination, this means that elements diagonal to each other (in a down-and-right direction) actually have similar electronegativity, and this is supported by observational evidence.



- Properties which may be supported by the diagonal relationship, which is most noticeable in Periods 2 and 3:
  - o Electronegativity
  - o Atomic radius
  - o Electrical conductivity (e.g. B and Si are semiconductors)
  - Acidic Hydrolysis (e.g. aqueous solutions of Be<sup>2+</sup> and Al<sup>3+</sup> are weakly acidic)
  - Nature of compounds (e.g. Be and A*l* both form covalent chlorides BeC*l*<sub>2</sub> and A*l*C*l*<sub>3</sub>)
- You may need to use this diagonal relationship to predict the properties of a given element.

# 4.3 Deduce identity of unknown element from given information

• It is also possible that you will be given certain information and asked to deduce the identity of an unknown element and its position in the Periodic Table. Cross-reference the information with what you know to identify the element.

Exercise 8			
An unknown element is found in	period 3. Identify this unknown element given the following		
information.			
• It has a melting point of 650 $^\circ$	<ul> <li>It has a melting point of 650 °C.</li> </ul>		
• The chloride is a white solid at room temperature. The chloride dissolves readily in water to			
form a slightly acidic solution with a pH of 6.5.			
Ans: Magnesium / Mg	<ul> <li>Thinking process: Use the provided data and match up with your knowledge of Periodicity.</li> <li>Which chlorides have high melting points?</li> <li>Which chloride forms solution with pH 6.5?</li> </ul>		

### 5. APPENDIX

'If you want to learn about the future, you have to look into the past.' The history of the periodic table and IUPAC demonstrates the gradual perfection of scientific research and the continuous effort for better communication to facilitate it. In the future, new tools will continue to help scientists in evermore exciting exploration of the elements, as well as in broader collaborations for the betterment of mankind.

Qi-Feng Zhou, President, International Union of Pure and Applied Chemistry (IUPAC)

#### Did you know?

On 20 December 2017, during its 74th Plenary Meeting, the United Nations (UN) General Assembly 72nd Session proclaimed 2019 as the International Year of the Periodic Table of Chemical Elements (IYPT 2019).

IYPT 2019 will coincide with the 150th anniversary of the discovery of the Periodic System by Dmitry Mendeleev in 1869. The events of IYPT aims to enhance the understanding and appreciation of the Periodic Table and chemistry in general among the public. Particular areas where the Periodic Table and its understanding have had a revolutionary impact are in nuclear medicine, the study of chemical elements and compounds in space and the prediction of novel materials.

#### Development of the periodic table

Dmitri Mendeleev proposed the periodic system in 1869. His Periodic Table, which arranged elements according to atomic mass, was widely accepted. It was able to predict the properties of five undiscovered elements and their compounds, which provided further proof of his periodic system.

However, there were some inconsistencies – Mendeleev placed argon (atomic mass 39.95) before potassium (atomic mass 39.10), which contradicted his principle of arranging elements according to atomic mass. Henry Moseley's subsequent work provided evidence that the arrangement of elements according to atomic number could explain these contradictions. This is the Periodic Table that is still in use today.

All elements from atomic numbers 1 (hydrogen) to 118 (<u>ununoctium</u>) have been discovered or synthesised. The four most recent elements (113, 115, 117 and 118) were fully added into the periodic table, with the approval of their names and symbols, on 28 November 2016.

#### Further reading

Royal Society of Chemistry: http://www.rsc.org/periodictable/history/about



International Union of Pure and Applied Chemistry: <u>https://iupac.org/what-we-</u> do/periodic-table-of-elements/



IYPT 2019: https://www.iypt2019.org/about-theperiodic-table



There are media (e.g. podcasts, videos) about the elements, fun activities and challenges to try out on the various websites.

What does the history and development of Periodic Table tell us about the Nature of Science?

- Science is an evidence-based, model-building enterprise concerned with the natural world.
- Scientific knowledge is reliable and durable, yet subject to revision in the light of new evidence.