

Pioneer Junior College
Higher 2 Chemistry (9647)
Inorganic Chemistry
The Periodic Table: Chemical Periodicity

Reference

- **Comprehensive Chemistry, Inorganic Chemistry 'HKAL Course'**

Content

- Periodicity of physical properties of the elements: variation with proton number across the third period (sodium to argon) of:
 - (i) atomic radius and ionic radius
 - (ii) melting point
 - (iii) electrical conductivity
 - (iv) ionisation energy
- Periodicity of chemical properties of the elements in the third period
 - (i) Reaction of the elements with oxygen and chlorine
 - (ii) Variation in oxidation number of the oxides (sodium to sulfur only) and of the chlorides (sodium to phosphorus only)
 - (iii) Reactions of these oxides and chlorides with water
 - (iv) Acid/ base behaviour of these oxides and the corresponding hydroxides

Learning Outcomes

Candidates should, for the third period (sodium to argon), be able to:

- describe qualitatively (and indicate the periodicity in) the variations in atomic radius, ionic radius, melting point and electrical conductivity of the elements (see the Data Booklet)
- explain qualitatively the variation in atomic radius and ionic radius
- interpret the variation in melting point and in electrical conductivity in terms of the presence of simple molecular, giant molecular or metallic bonding in the elements
- explain the variation in first ionisation energy
- describe the reactions, if any, of the elements with oxygen (to give Na_2O ; MgO ; Al_2O_3 ; P_4O_{10} ; SO_2 ; SO_3), and chlorine (to give NaCl ; MgCl_2 ; AlCl_3 ; SiCl_4 ; PCl_5)
- state and explain the variation in oxidation number of the oxides and chlorides
- describe the reactions of the oxides with water
[treatment of peroxides and superoxides is not required]
- describe and explain the acid/ base behaviour of oxides and hydroxides, including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids
- describe and explain the reactions of the chlorides with water
- interpret the variations and trends in (f), (g), (h), and (i) in terms of bonding and electronegativity
- suggest the types of chemical bonding present in chlorides and oxides from observations of their chemical and physical properties

In addition, candidates should be able to:

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

I Introduction

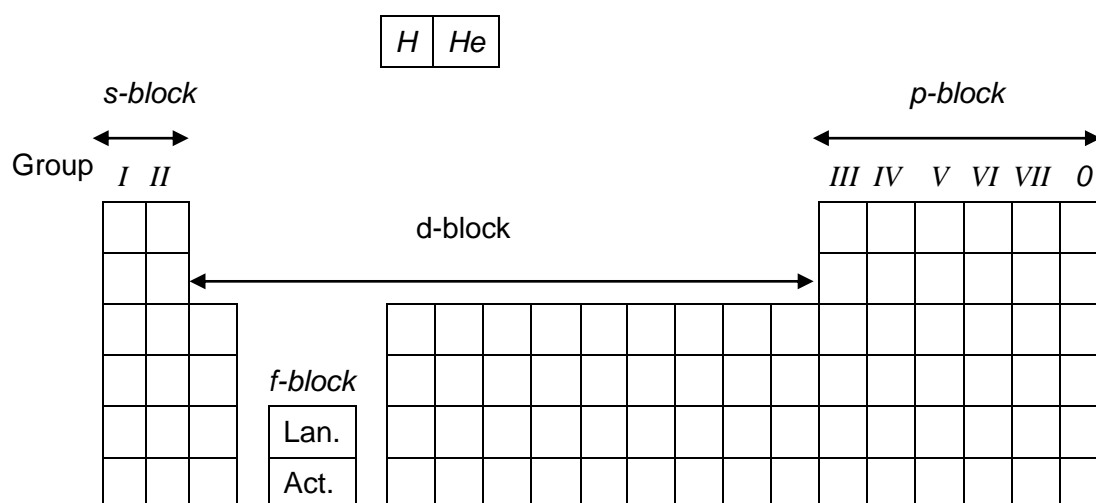
In the Periodic Table:

- Elements are arranged in order of increasing atomic number.
- **Groups** are vertical columns containing **elements with similar properties**.
- **Periods** are horizontal rows across which **trends in properties** are shown. Properties vary in a fairly regular way across a period from left to right. The pattern is then repeated across the next period. **The recurrence of periodic patterns is called periodicity.**

e.g. Period 2 Metals → Non-Metals

Period 3 Metals → Non-Metals

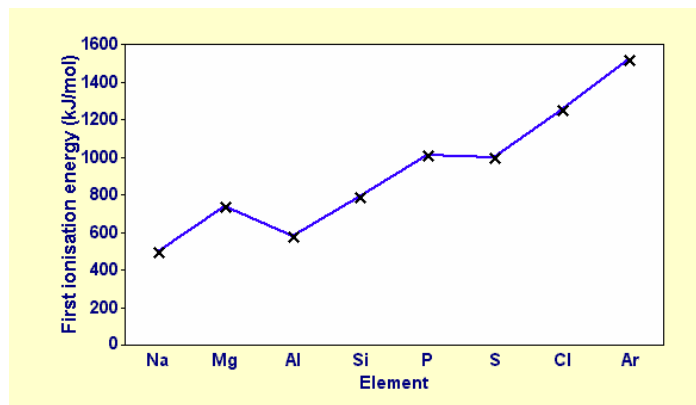
Key areas in the Periodic Table



- Areas of the table are labelled s-block, p-block, d-block & f-block.
- Elements in the s-block have their highest energy electrons in the s orbitals.
e.g. Li ($1s^2 2s^1$)
- Elements in the p-block have their highest energy electrons in the p orbitals.
e.g. C ($1s^2 2s^2 2p^2$)

II Periodicity of Physical Properties of the Elements

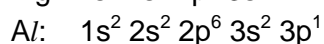
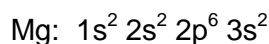
(A) Variation in first ionisation energy



Across the 3rd period, 1st I.E. generally increases.

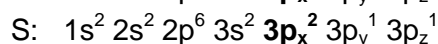
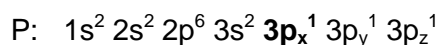
- There is an increase in nuclear charge but roughly the same shielding effect (**same number of inner shell electrons**)
- Hence, effective nuclear charge increases across the period. The valence (outermost) electrons are more strongly attracted to the nucleus. Hence, more energy is needed to remove the outermost electrons.

Anomaly 1: 1st I.E. of Mg > 1st I.E. of Al



This is because the valence electron of Al to be removed is from the 3p orbital which is of higher energy and further away from the nucleus compared to valence electron in the 3s orbital of Mg. As the valence electron of Al is further and more weakly attracted to the nucleus, it is more easily removed and requires less energy.

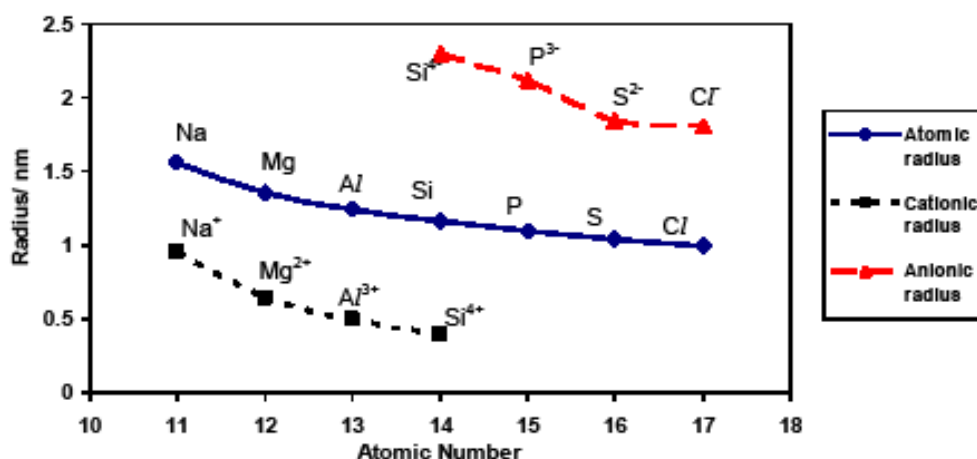
Anomaly 2: 1st I.E. of P > 1st I.E. of S



The pair of electrons in the same 3p_x orbital of S gives rise to inter-electron repulsion. Thus, it is easier to remove one of the paired electron in 3p_x orbital of S, this requires less energy compared to removing an unpaired electron of P.

(B) Variation in atomic radius

1. The atomic radii of the elements depend on the attraction between the positively charged nuclei and its outermost electron cloud. The greater the attraction, the smaller the radii.
2. The atomic radii of the elements decrease across period 3 gradually. Across a period, there is an increase in the effective nuclear charge, due to increasing number of protons in the nucleus and approximately constant shielding effect.

(C) Variation in ionic radius

1. The cationic radius decreases from Na⁺ to Si⁴⁺. (Electronic configuration: 1s² 2s² 2p⁶)
 - Nuclear charge increases from Na⁺ to Si⁴⁺ due to an increase in protons.
 - Shielding effect remains approximately constant as these cations are isoelectronic.
 - Due to the increase in nuclear charge, the valence electrons in these ions are held more tightly to the nucleus, accounting for a smaller cationic radius.
2. The anionic radius decreases from Si⁴⁻ to Cl⁻ (Electronic configuration: 1s² 2s² 2p⁶ 3s² 3p⁶)
 Similarly for the anions (Si⁴⁻, P³⁻, S²⁻ and Cl⁻) are isoelectronic (constant shielding). The decrease in anionic radii is also due to the increase in nuclear charge.



Why are the ionic radii of anions greater than that of cations for elements of the same period?

Radii of anions > Radii of cations because of an **extra shell** of electrons in the anions.

e.g. electronic configuration of

Na ⁺	: 1s ² 2s ² 2p ⁶
P ³⁻	: 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶

Exercise 1

The table below shows the radii of some Period 3 elements in their ionic forms.

Ions	Na^+	Mg^{2+}	Al^{3+}	Si^{4-}	P^{3-}	S^{2-}	Cl^-
Radii / nm	0.095	0.065	0.050	0.271	0.212	0.184	0.181

- (a) Explain the variation of radius for the above ions.

Na^+ to Al^{3+} are isoelectronic. Si^{4-} to Cl^- are isoelectronic. For both cations and anions that are isoelectronic, ionic radii decrease because of increasing nuclear charge and constant shielding.

- (b) What would you predict about the size of the K^+ ion relative to the Cl^- ion?

K^+ and Cl^- are isoelectronic. K^+ has a smaller radius because of a larger nuclear charge.

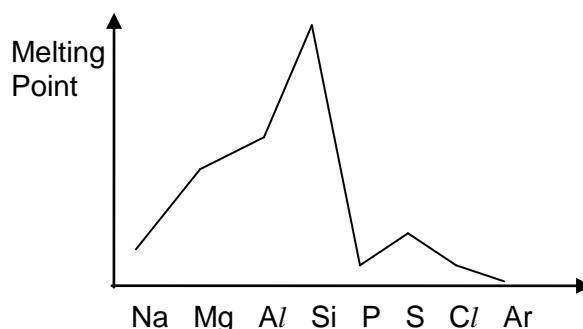
- (c) What would you predict about the size of the Si^{4+} ion relative to the Si^{4-} ion? Give your reason.

Si^{4+} is smaller than Si^{4-} . Both have the same number of protons. However, more electrons of Si^{4-} resulted in repulsion between the valence electrons, increasing the ionic radius. The valence electrons in Si^{4-} are also occupying another quantum shell. Shielding effect of the inner shell is greater in Si^{4-} than in Si^{4+} .

(D) Variation in melting points

- Melting point depends on the strength of the attractive forces between the particles at the lattice points and the extent to which these forces have to be broken for the solid to change to liquid. For metallic and ionic bonds, the process of melting simply weakens the bonds; whereas for covalent bonds in giant covalent structure, the process of melting breaks the covalent bonds completely.

- Period 3 elements:



Giant metallic structures

- Na, Mg and Al have giant metallic structures with strong metallic bonds. A large amount of energy is needed to overcome these bonds, hence they have high m.p.
- There is an increase in m.p. from Na to Al because there is an increase in the number of valence electrons donated to the delocalised electron cloud (in the “sea of delocalised electrons”), and an increase in the charge density of cations due to increasing cationic charge but decreasing cationic size. So, metallic bond strength increases from Na to Al.

Giant molecular structure

- Si has a giant molecular structure with very strong covalent bonds between Si atoms. A large amount of energy is needed to break these bonds; hence the melting point is the highest.

Simple molecular structures

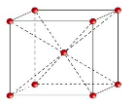
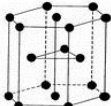
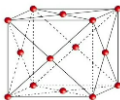
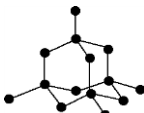
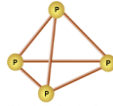
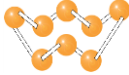


- P, S, Cl and Ar have simple molecular structures with weak inter-molecular van der Waals' forces. Less energy is needed to overcome them, hence the m.p are low.

Of the four, S₈ has the highest m.p as van der Waals' forces are determined by the number of electrons in the molecule. (The more electrons, the larger electron cloud to be polarised). (Hence, m.p. S₈ > m.p. P₄ > m.p. Cl₂ > m.p. Ar.)

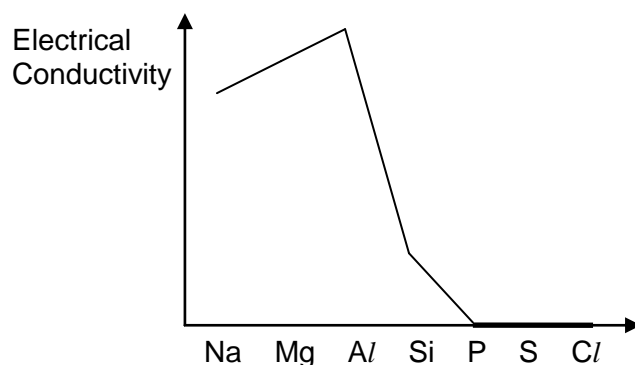
Na Mg Al Si
 ← giant structures →

P₄ S₈ Cl₂ Ar
 ← simple molecular structures →

- Boiling point, ΔH_{fus} (enthalpy change of fusion; solid to liquid) and ΔH_{vap} (enthalpy change of vapourisation; liquid to gas) follow similar trends as the melting point with the same reasons as discussed above.
- Summary: Periodic Trend of Variation in Structure and Bonding of the Elements

Elements	Na	Mg	Al	Si	P (P ₄)	S(S ₈)	Cl (Cl ₂)	Ar
m.p. / °C	98	650	660	1414	44 (white P)	115	-102	-189
Structure					 <small>Molecule of yellow phosphorus</small>			
Type of Structure	giant metallic lattice			giant covalent molecular	simple covalent molecular			Simple atomic
Bonding	strong metallic bond			strong covalent bond	intermolecular weak van der Waals' forces between molecules (but intramolecular strong covalent bonds exist within each molecule)			weak van der Waals' forces
	• the metallic bonds (strong electrostatic forces between the positive ions and mobile valence electrons) are being <u>weakened</u> when solid changes to liquid - not completely "broken"			• the strong covalent bonds between Si atoms are being <u>broken</u> completely	• within each molecule, atoms are held by strong covalent bonds; between molecules (or atoms for argon), weak intermolecular forces of attraction hold the molecules together. • the weak vdW can be easily overcome/ <u>weakened</u>			
Remarks	• m.p. increases across the period from Na to Al due to: (i) an <u>increase</u> in the number of valence electrons donated to the delocalised electron cloud which strengthens the metallic bond (ii) <u>increase in charge density of cation</u> (charge density $\propto \frac{\text{charge}}{\text{radius}}$; increase cationic charge but decrease cationic size)				• <u>m.p.(S₈) > m.p.(P₄) > m.p.(Cl₂) > m.p.(Ar) as M_r(S₈) > M_r(P₄) > M_r(Cl₂) > M_r(Ar).</u> • The decrease in M _r from S ₈ to Ar means that the <u>electron cloud</u> decreases in size. Hence, there are lesser electrons to be polarised from S ₈ to P ₄ to Cl ₂ to Ar, which results in weaker vdW. • S ₈ has the highest m.p. since it has the greatest M _r and hence there are <u>more electrons</u> to be polarised. Thus vdW forces between its molecules.			
Melting point	High, increasing from Group I to Group III			Highest	Very low			

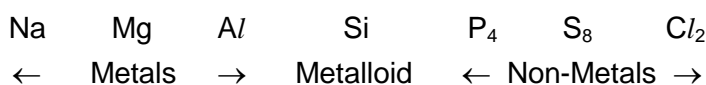
(E) Variation in electrical conductivity



1. Na, Mg and Al are metals. They have metallic structures made up of a regular lattice of cations in a sea of delocalised and mobile electrons which move in one direction when a potential difference is applied. Hence, their electrical conductivities are high.

Conductivity increases from Na to Al due to an increase in the number of valence electrons donated to the delocalised electron cloud by the metal atoms.

2. Si is a metalloid (having both properties of metals and non-metals). It has low conductivity. It is a semi-conductor.
3. P, S and Cl are non-metals. The electrons are localised in covalent pairs and are unable to move to conduct electricity. They have very low conductivities. They are non-conductors (insulators).



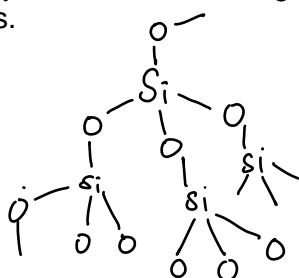
Exercise 2

The elements across the third period are as follow:



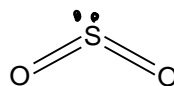
Which of these elements

- (i) exist as diatomic molecules at room temperature and pressure, **Cl**
 - (ii) has the largest first ionisation energy, **Ar**
 - (iii) has the highest electrical conductivity, **Al**
 - (iv) has the highest melting point in its oxide form? **Mg**
- (a) Two of the elements from the period form covalent oxides with formulae of the type XO₂. Draw displayed formulae showing the bonding of the two oxides, and suggest values for the bond angles.



Si-O-Si bond angle: **104.5°**

O-Si-O bond angle: **109.5°**



O-S-O bond angle: **slightly < 120°**

III Periodic Variation of Chemical Properties of the Elements

(A) Reaction with O₂

Period 3 Elements	Equations	Observation
Na	$4\text{Na(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Na}_2\text{O(s)}$	Burns in O ₂ , very vigorous with a yellow flame, leaving behind a white residue of Na ₂ O.
Mg	$2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$	Burns very vigorously in O ₂ with a bright white flame, leaving behind a white residue to MgO.
Al	$4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$	Al ₂ O ₃ (s) formed on the surface
Si	No reaction	SiO ₂ (s) is formed when Si(s) is heated in O ₂ (g) at about 400°C
P	In limited oxygen, $\text{P}_4\text{(s)} + 3\text{O}_2\text{(g)} \rightarrow \text{P}_4\text{O}_6\text{(s)}$ In excess oxygen, $\text{P}_4\text{(s)} + 5\text{O}_2\text{(g)} \rightarrow \text{P}_4\text{O}_{10}\text{(s)}$	P ₄ burns with a white flame, producing white smoke – a mixture of P ₄ O ₆ and P ₄ O ₁₀ .
S	$\text{S(s)} + \text{O}_2\text{(g)} \rightarrow \text{SO}_2\text{(g)}$ [S ₈ can be used to replace S] $\text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{SO}_3\text{(l)}$	S burns in O ₂ with a blue flame to give SO ₂ (g). Note: SO ₃ is not formed during combustion of sulfur. It is only formed in the Contact process using V ₂ O ₅ catalyst and a temperature of 450°C.

(B) Reaction with Cl₂

Period 3 Elements	Equations	Observation
Na	$2\text{Na(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{NaCl(s)}$	Burns with an orange flame, leaving behind a white residue of NaCl.
Mg	$\text{Mg(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{MgCl}_2\text{(s)}$	Burns with a bright white flame, giving a white residue of MgCl ₂ .
Al	$2\text{Al(s)} + 3\text{Cl}_2\text{(g)} \rightarrow \text{Al}_2\text{Cl}_6\text{(g)}$	Burns with a white flame, forming white fumes of Al ₂ Cl ₆ .
Si	$\text{Si(s)} + 2\text{Cl}_2\text{(g)} \rightarrow \text{SiCl}_4\text{(l)}$	Reacts slowly to form a colourless liquid.
P	$\text{P}_4\text{(s)} + 6\text{Cl}_2\text{(g)} \rightarrow 4\text{PCl}_3\text{(l)}$ $\text{PCl}_3\text{(l)} + \text{Cl}_2\text{(g)} \rightarrow \text{PCl}_5\text{(s)}$	Forms a mixture of 2 chlorides: a colourless liquid (PCl ₃) and a yellow solid (PCl ₅).

IV Properties of Oxides of Period 3 Elements

(A) Formula, Physical Properties, Structure and Bonding of Oxides of Na to P

Group	I	II	III	IV	V	VI
Period 3	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀ P ₄ O ₆	SO ₃ , SO ₂
m.p / °C	1132	2852	2072	1650	340 24	17 -76
Physical state of oxide at 20°C	Solid					Liquid, Gas
Conduction of electricity by molten or liquid oxide	Good			Nil	Nil	
Structure and Bonding	Giant ionic lattice with strong electrostatic forces of attractions between ions			Giant molecular structure with strong covalent bonds between Si and O atoms	Simple molecular structure with weak van der Waals forces between the molecules	

1. Metallic oxides are all ionic. All non-metallic oxides form simple molecular structures except for SiO₂ which has a giant molecular structure.
2. Melting points of Na₂O, MgO and Al₂O₃ are high because a lot of energy is required to weaken the strong ionic bonds between oppositely charged ions, within the giant ionic structures. Thus, they conduct electricity well in molten state due to presence of mobile ions as charge carriers.
3. For SiO₂, it has strong covalent bonds between the Si and O atoms. A lot of energy is required to break the bonds in the giant structure, thus it has very high melting points. Due to the absence of mobile charged particles, it does not conduct electricity.
4. Oxides of P and S exist as simple discrete molecules which are held together by weak van der Waals forces. Thus, less energy is required to overcome these weak forces between the molecules, they have relatively low melting points. Like SiO₂, they do not conduct electricity in solid or molten states due to the absence of mobile charge carriers.

(B) Variation in oxidation number of the oxides of Na to P

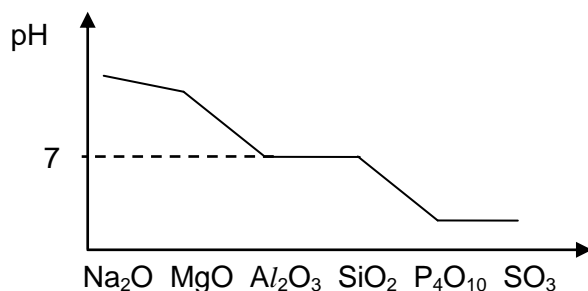
Oxide name	Formula	Oxidation number of Period 3 element	Highest oxidation state
Sodium oxide	Na ₂ O	+1	+1
Magnesium oxide	MgO	+2	+2
Aluminium oxide	Al ₂ O ₃	+3	+3
Silicon(IV) oxide (or silicon dioxide)	SiO ₂	+4	+4
Phosphorus(III) oxide (or phosphorus trioxide)	P ₄ O ₆	+3	+5
Phosphorus(V) oxide (or phosphorus pentoxide)	P ₄ O ₁₀	+5	
Sulfur dioxide	SO ₂	+4	+6
Sulfur trioxide	SO ₃	+6	

- The highest oxidation number is the group number of the Period 3 elements as it reflects the number of valence electrons available for bonding.
- The oxidation numbers of the Period 3 elements in their oxides are always positive because O is more electronegative than any of the Period 3 elements.
- P and S show several oxidation numbers because they can expand their octet structures by the excitation of the valence electrons into [low lying vacant 3d orbitals](#).

(C) Reaction of Oxides of Na to P with Water

Element	Oxides	Reactions	Remarks	pH of solution
Na	Na ₂ O (basic)	Na ₂ O(s) + H ₂ O(l) → 2 NaOH(aq)	reacts vigorously to give alkaline solution	about 13
Mg	MgO (basic)	MgO(s) + H ₂ O(l) ⇌ Mg(OH) ₂ (s) Mg(OH) ₂ (s) + aq ⇌ Mg ²⁺ (aq) + 2OH ⁻ (aq)	slightly soluble to give <u>weakly</u> alkaline solution	about 9
Al	Al ₂ O ₃ (amphoteric)	<u>insoluble</u> in water, no reaction		about 7
Si	SiO ₂ (acidic)			
P	P ₄ O ₆ (acidic)	P ₄ O ₆ (s) + 6 H ₂ O(l) → 4 H ₃ PO ₃ (aq)	reacts to give strong <u>dibasic</u> phosphorous acid	about 2
	P ₄ O ₁₀ (acidic)	P ₄ O ₁₀ (s) + 6 H ₂ O(l) → 4 H ₃ PO ₄ (aq)	reacts to give strong <u>tribasic</u> phosphoric acid	
S	SO ₂ (acidic)	SO ₂ (g) + H ₂ O(l) → H ₂ SO ₃ (aq)	reacts to give strong dibasic sulfurous acid	
	SO ₃ (acidic)	SO ₃ (g) + H ₂ O(l) → H ₂ SO ₄ (aq)	reacts to give strong dibasic sulfuric acid	

- Variation in the pH of the solutions produced when the highest oxides of the elements Na to S are separately added to water:

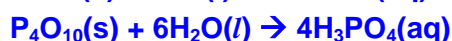
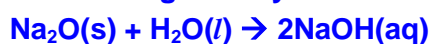


Exercise 3

Explain the trend of the resulting solution pH when oxides of the elements react with water. Write an equation each for an oxide that forms acidic solution and another that forms alkaline solution with water.

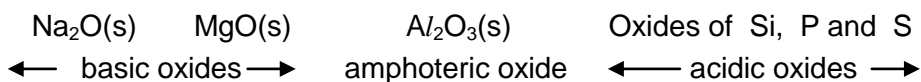
When oxides of Period 3 elements react with water, the resulting pH decreases from oxides of Na to S.

Metallic oxides are generally acidic and non-metallic oxides are generally basic.



(D) Acid/ Base Behaviour of Oxides

Elements	Oxides	Acid/ Base Character	Reactions
Na	Na ₂ O	basic (reacts with acid to form salts and water)	$\text{Na}_2\text{O}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Mg	MgO		$\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Al	Al ₂ O ₃	amphoteric (reacts with both acids and alkalis)	$\text{Al}_2\text{O}_3(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$ $\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}[\text{Al}(\text{OH})_4](\text{aq})$
Si	SiO ₂	acidic (reacts with base form salts and water)	No reaction with dilute NaOH(aq). [Reaction with concentrated NaOH at high temperature: $\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$]
P	P ₄ O ₆		$\text{P}_4\text{O}_6(\text{s}) + 8\text{NaOH}(\text{aq}) \rightarrow 4\text{Na}_2\text{HPO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
	P ₄ O ₁₀		$\text{P}_4\text{O}_{10}(\text{s}) + 12\text{NaOH}(\text{aq}) \rightarrow 4\text{Na}_3\text{PO}_4(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
S	SO ₂		$\text{SO}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
	SO ₃		$\text{SO}_3(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$



Across Period 3, the nature of the oxides changes from basic through amphoteric to acidic. This is because electronegativity of the elements increases, resulting in the electronegativity difference between oxygen and the elements to decrease. Hence, as the elements change from metals to non-metals, bonding of their oxides varies from ionic to covalent.

Exercise 4

- (a) Which element forms an amphoteric oxide? **Al**
- (b) Write equations to show the reaction of this oxide with:

- (i) dilute sulfuric acid



- (ii) dilute potassium hydroxide.



Exercise 5

MgO , Al_2O_3 and SiO_2 exist as white solids. If a sample of one of the oxides was provided as a white powder, describe the reactions you could carry out on the powder to determine which of the three oxides it was.

Divide the sample into three portions in separate test tubes.

- To the first portion, add water.
- To the second portion, add dilute hydrochloric acid.
- To the last portion, add dilute sodium hydroxide.

Note the solubility of the sample in each case.

If the sample is soluble in dilute hydrochloric acid, but insoluble in water or dilute sodium hydroxide, then it is MgO . If the sample is soluble in dilute hydrochloric acid and dilute sodium hydroxide but insoluble in water, then it is Al_2O_3 . If the sample is insoluble in water, dilute hydrochloric acid and dilute sodium hydroxide, it is SiO_2 .

Examiners' comments: This was a testing part, requiring candidates to use their knowledge of the acid-base properties of the period 3 oxides. They tended not to score highly. Many thought that MgO was soluble in water, giving a (clear) alkaline solution, and many also thought that SiO_2 would react with NaOH(aq) , suggesting perhaps, a lack of experience of practical chemistry. (Warming NaOH(aq) in a silica-glass test tube would be highly dangerous if it caused the test tube to dissolve.)

Exercise 6

In each of the following reactions, describe the way in which the oxide of the named element is reacting and discuss whether its behaviour is what you would expect from the position of the element in the Periodic Table.

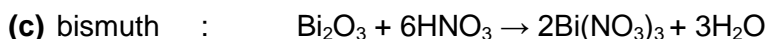


SiO_2 is reacting as an acidic oxide in the above reaction. Silicon, a Group IV element, is a non-metal. It forms an oxide which is covalent and hence it is expected to be acidic in nature.



BeO is reacting as an acidic oxide in the above reaction. Beryllium, a Group II element, is a metal. Its oxide is expected to be basic.

However, due to its small cationic size and relatively high charge, the oxide ion is polarised significantly, thus showing substantial covalency. It is, therefore amphoteric, and shows acidic behaviour towards alkalis.



Bi_2O_3 is reacting as a basic oxide. Bismuth is a Group V element and its oxide is expected to be acidic. However due to its large size and low electronegativity, its oxide is predominantly ionic, hence it shows basic behaviour towards acids.

Examiners' comments: This part stumped many candidates, who often claimed that the reactions were redox ones (without, however, showing how they had calculated the 'change' in oxidation number of the element concerned). Candidates were expected to relate basicity / acidity to the element's Group or metallic / non-metallic property. Thus, (a) was 'expected', but (b) and (c) were not.

(E) Summary of properties of oxides

Element	Na	Mg	Al	Si	P	S
Formula of Oxide	Na ₂ O Na ₂ O ₂	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ P ₄ O ₁₀	SO ₂ SO ₃
Oxidation number of element	+1	+2	+3	+4	+3 +5	+4 +6
Structure	giant ionic lattice			giant molecular structure	simple molecular structure	
Bonding	(ionic)	MgO (ionic, with slight covalent character)	Al ₂ O ₃ (ionic, with significant degree of covalent nature)	strong covalent bonds	weak intermolecular van der Waals' forces	
Effect of H ₂ O on Oxides	dissolves to form strong alkali NaOH	sparingly soluble forms weak alkali Mg(OH) ₂	insoluble		reacts to form strong acids	
pH of aqueous solution	13	9	7		2	
Nature of Oxides	Basic		Amphoteric	Acidic		

V Properties of Chlorides of Period 3 Elements

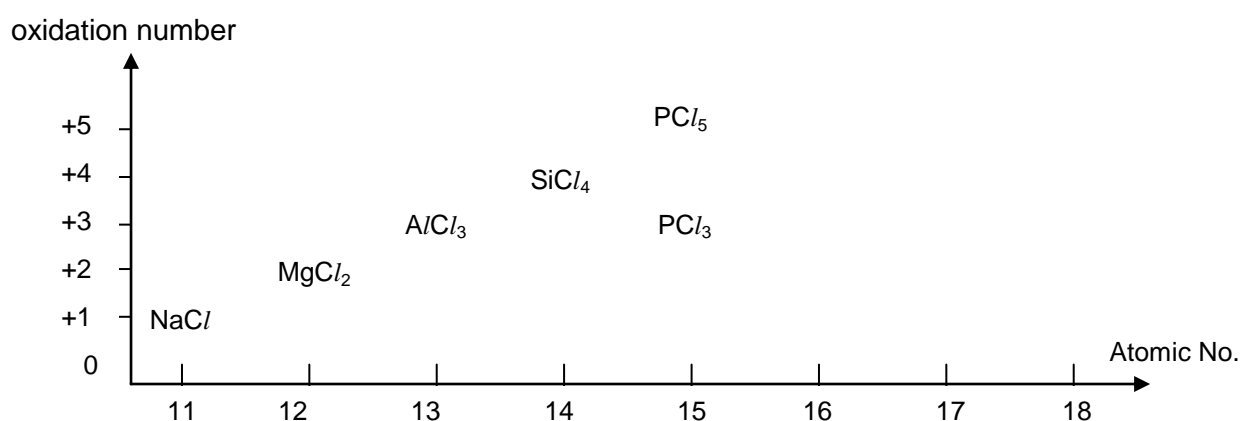
(A) Formula, Structure and Bonding of Chlorides of Na to P

Group	I	II	III	IV	V
Period 3	NaCl	MgCl ₂	AlCl ₃ (or Al ₂ Cl ₆)	SiCl ₄	PCl ₃ , PCl ₅
Melting point / °C	801	714	(sublimes at 178)	-69	-94 167
Physical state of chloride at 20°C	Solid			Liquid	Liquid, Solid
Electrical conductivity in molten or liquid state	good (presence of mobile ions in molten and aqueous)		very poor	Nil	
Structure and Bonding	giant ionic lattice structure		simple covalent molecular; intramolecular covalent bond and intermolecular van der Waals' forces		

- Although Al is a metal, its chlorides are essentially covalent. This is because Al³⁺ has small size and is highly charged, (Chargedensity $\propto \frac{\text{charge of cation}}{\text{cationic radius}}$)

∴ it has high charge density. Cl⁻, on the other hand, has large electron cloud. Hence, Al³⁺ polarise the large electron cloud of Cl⁻ to large extent. This results in sharing of electrons, thus AlCl₃ exists as covalent compound.
- AlCl₃ sublimes at 178 °C to give Al₂Cl₆(g) dimer which dissociates to the monomer AlCl₃(g) at higher temperature.

(B) Variations in Oxidation Number of the Chloride of Na to P



- The oxidation numbers of the Period 3 elements in their chlorides are always positive because Cl is more electronegative than any of the Period 3 elements.
- The maximum oxidation number of each element in its chlorides is the same as the number of valence electrons of that element.
- (e.g. PCl₃ and PCl₅) can show several oxidation states by expanding their octet structure using energetically accessible low lying vacant 3d orbitals for bonding.

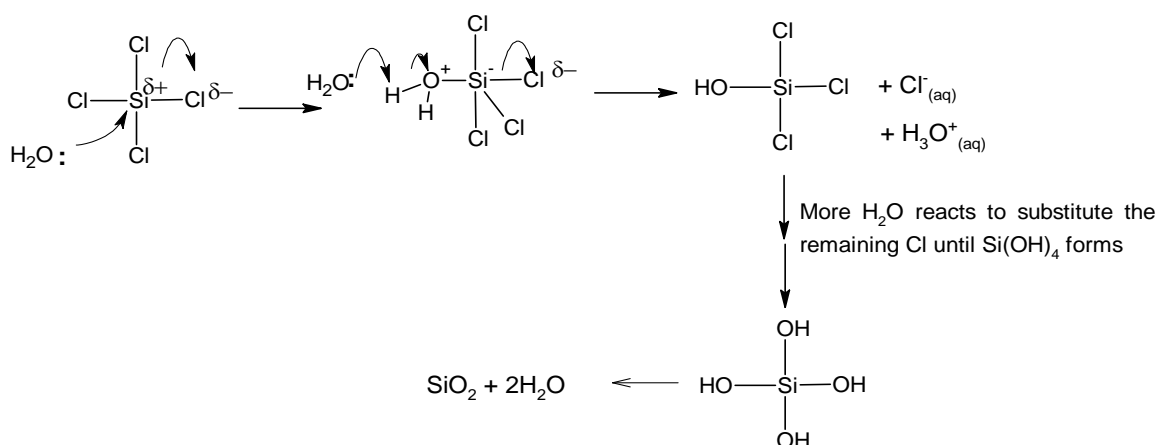
(C) Reactions of Chlorides of Na to P With Water

Element	Chloride	Reactions	Remarks	pH of solution
Na	NaCl	$\text{NaCl(s)} + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	dissolves readily, no hydrolysis	7
Mg	MgCl ₂	Dissolution $\text{MgCl}_2(\text{s}) + \text{aq} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq})$ Hydrolysis $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+(\text{aq}) + \text{H}^+(\text{aq})$	dissolves readily, slight hydrolysis	about 6.5
Al	AlCl ₃	Dissolution $\text{AlCl}_3(\text{s}) + 6 \text{H}_2\text{O(l)} \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3 \text{Cl}^-(\text{aq})$ Hydrolysis: $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}^+(\text{aq})$	dissolves and hydrolyse; Al ³⁺ has high charge density, able to polarise, weaken and break O-H bond in H ₂ O of [Al(H ₂ O) ₆] ³⁺ (aq) to release H ⁺ ions.	3
Si	SiCl ₄	$\text{SiCl}_4(\text{l}) + 4 \text{H}_2\text{O(l)} \rightarrow \text{SiO}_2 \cdot 2 \text{H}_2\text{O(s)} + 4 \text{HCl(aq)}$	chlorides hydrolyse in water to form acidic solution of HCl	1 to 2
P	PCl ₃	$\text{PCl}_3(\text{l}) + 3 \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_3(\text{aq}) + 3 \text{HCl(aq)}$		
	PCl ₅	<u>With a limited supply of water (usually cold)</u> $\text{PCl}_5(\text{s}) + \text{H}_2\text{O(l)} \rightarrow \text{POCl}_3(\text{s}) + 2 \text{HCl(aq)}$ <u>With large amount of water</u> $\text{PCl}_5(\text{s}) + 4 \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5 \text{HCl(aq)}$		

- Typical ionic chlorides simply dissolve into its ions in water, without undergoing hydrolysis. Typical covalent chlorides generally undergo hydrolysis and react with water.

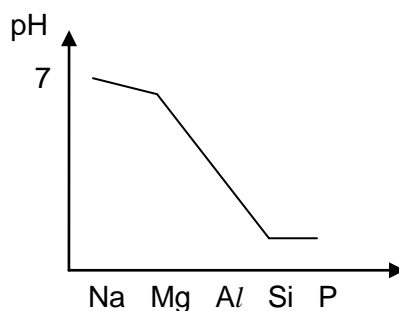


Explain why SiCl₄ hydrolyse to form HCl but CCl₄ does not? (for your information only)



Due to the presence of vacant 3d orbitals in Si, it is able to attract H_2O molecule and accept a lone pair of electron from the O atom, forming $\text{Si}(\text{OH})_4$. As it is not stable, $\text{Si}(\text{OH})_4$ will decompose to SiO_2 .

Variation in pH of the solutions produced when the chlorides of the Period 3 elements are added to water:



(D) Summary of Properties of Chlorides

Element	Na	Mg	Al	Si	P
Formula of Chloride	NaCl(s)	MgCl ₂ (s)	AlCl ₃ (s)	SiCl ₄ (l)	PCl ₃ (l) PCl ₅ (s)
Oxidation number of element	+1	+2	+3	+4	+3 +5
Structure	giant ionic lattice		simple molecular structure		
Bonding	Structure: Giant ionic lattice Attraction overcome: Strong ionic bonds (MgCl ₂ has slightly covalent nature)		Structure: simple covalent molecules Attraction overcome: weak van der Waals' forces		
Melting Point	very high		sublimes at 178 °C, forms Al ₂ Cl ₆ (g)	low	
Effect of H ₂ O on Chlorides	dissolves (except for slight hydrolysis of MgCl ₂)		hydrolysis occurs		
pH of aqueous solution	7	about 6.5	3	1 to 2	

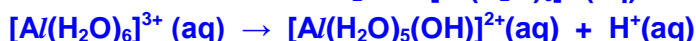
Exercise 7: Chlorides

- (a) By using $AlCl_3$ as an example, explain how hydrolysis takes place to form an acidic solution when $AlCl_3$ reacts with water.

$AlCl_3$ first hydrolysed / dissolved / ionised in water.



Al^{3+} has a very high charge density. As it is very polarising, it is able to polarise, weaken and break O-H bond in H_2O of $[Al(H_2O)_6]^{3+}(aq)$ to release H^+ ions. $pH = 3$



Exercise 8: Chlorides

Periodicity is the reoccurring of similar patterns across the periods of the Periodic Table. Period 2 and Period 3 show similar trends of periodicity. The elements in their chloride forms across the second period are as shown:



- (a) How is the type of bonding in the chlorides of the elements in Period 2 related to their electronegativities?

Bonding in the chloride changes from ionic to covalent as electronegativities of Period 2 elements increases, leading to a decrease in difference in electronegativity between chlorine and Period 2 element.

- (b) Predict the variation in boiling points of the elements in their chloride forms across the period. Explain your reasons.

Boiling points of the chlorides generally decreases across the period as the bonding and structure of the chlorides changes from giant ionic lattice with strong ionic bonds between the ions to simple molecular structure with weak van der Waals forces between the molecules.

- (c) Predict the variation in electrical conductivity of the elements in their chloride forms across the period.

Only $LiCl$ is able to conduct electricity in the molten state because of the presence of mobile ions. The rest of the chlorides are covalent with electrons localised in covalent bonds or lone pairs. Without mobile charge carriers, they are unable to conduct electricity.

- (d) How would you expect $LiCl$ and BCl_3 to behave when added to water?

$LiCl$ will dissolve readily in water, undergoing very slight hydrolysis due to its high charge density (diagonal relationship with Mg). BCl_3 undergoes hydrolysis in water to form an acidic solution (boric acid and hydrochloric acid).

VI Other Trends Across Periods

(A) Electronegativity

- It is measure of the relative tendency of an atom to attract the bonding pair of electrons in a covalent bond.
- Electronegativity increases across a period. This is due to a simultaneous increase in the nuclear charges with constant screening effect.
- Electronegativity difference is related to bonding:

Electronegativity Difference between 2 atoms	Bonding
great (> 1.85)	Ionic
in between (0.4 – 1.85)	Intermediate (ionic / covalent)
small (<0.4)	Covalent

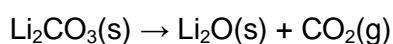
Compounds of Period 3 elements	Na	Mg	Al	Si, P
Oxides	Ionic	Ionic	Ionic	Covalent
Chlorides			Covalent (with ionic character)	

(B) Diagonal Relationships

- Since electronegativity increases across the periods and decreases down the groups and atomic size decreases across the periods and increases down the groups, elements which are diagonally placed will have very similar atomic size and electronegativity resulting in similar physical and chemical properties.
- Electronegativities values:

roup	I	II	III	IV
Period 2 Elements	Li (1.0)	Be (1.5)	B (2.0)	-
Period 3 Elements	-	Mg (1.2)	Al (1.5)	Si (1.8)

- Hence,
 - Compounds of Li is similar to Mg:
Group I carbonates (e.g. Na_2CO_3 & K_2CO_3) are stable to heat. Li_2CO_3 , however undergoes thermal decomposition easily which resembles the behaviour of Group II carbonates.



This anomaly can be attributed to Li^+ having a higher charge density than other Group I cations.

Note: This is thermal decomposition, NOT combustion, so do not add $\text{O}_2(\text{g})$ as a reactant.

- Compounds of Be is similar to Al:
 BeCl_2 and AlCl_3 have similar chemical properties
 BeO and Al_2O_3 are amphoteric oxides.
- B is similar to Si:
Both elements are metalloids.

Note:

When answering questions, unless otherwise stated, all state symbols of balanced equations in this chapter need **not** be written. If written, they need to be correct.

VII Summary

1. Periodicity of Physical Properties of the Elements in Period 3

Period 3 elements	Na	Mg	Al	Si	P	S	Cl	Ar
Nature of elements	Metal			Metalloid	Non-metal			
Bonding in element	Metallic $\xrightarrow{\text{Covalent character increases}}$ Covalent							
Structure in element	Giant metallic lattice		giant covalent molecular		Simple molecular			
Atomic radii	$\xrightarrow{\text{Decreases across the period}}$							
Ionic radii (of isoelectronic ions)	$\xrightarrow{\text{Decreases across the period}}$							
Melting/ Boiling points	High and increasing from Na to Si				Low and $\text{S}_8 > \text{P}_4 > \text{Cl}_2 > \text{Ar}$			
Electrical conductivity	High and increasing from Na to Al		Semi-conductor		Nil			
1 st ionisation energy	$\xrightarrow{\text{Increases across the period (with 2 abnormalities)}}$							

2. Oxides of Na to S: Physical and Chemical Properties

Period 3 elements	Na	Mg	Al	Si	P	S
Bonding in oxides	Ionic $\xrightarrow{\text{Covalent character increases}}$ Covalent					
Structure in oxides	Giant ionic lattice			Giant covalent molecular	Simple molecular	
Max. oxidation number in oxides	$\xrightarrow{\text{Increases across the period}}$					
Electrical conductivity (molten)	Decrease from ionic to covalent oxides High $\xrightarrow{\hspace{1cm}}$ Nil Nil					
Effect of water on oxides	Acidity of resulting solution increases (pH drops) $\xrightarrow{\hspace{1cm}}$ forms alkaline solution $\text{Al}_2\text{O}_3, \text{SiO}_2$ (pH =7) forms acidic solution					

3. Chlorides of Na to P: Physical and Chemical Properties

Period 3 elements	Na	Mg	Al	Si	P
Bonding in chlorides	Ionic <div>Covalent character increases</div> Covalent				
Structure in chlorides	Giant ionic lattice		Simple molecular		
Max. oxidation number in oxides	Increases across the period				
Electrical conductivity	High <div>Decrease from ionic to covalent chlorides</div> Nil				
Effect of water on chlorides	NaCl/ <div>Acidity of resulting solution increases</div> forms neutral solution forms acidic solution				