

# CHAPTER 10: Chemical Periodicity

- 10.1 Periodicity in Physical Properties
- 10.2 Periodicity in Chemical Properties
- 10.3 Period 3 Oxides
- 10.4 Period 3 Chlorides

## Learning outcomes:

- (a) 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).
- (b) explain qualitatively the variation in atomic radius and ionic radius.
- (c) 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.
- (d) explain the variation in first ionisation energy.
- (e) describe the reactions, if any, of the elements with oxygen (to give  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ), chlorine (to give  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{SiCl}_4$ ,  $\text{PCl}_5$ ) and water (Na and Mg only).
- (f) state and explain the variation in oxidation number of the oxides and chlorides in terms of their valence shell electrons.
- (g) describe the reactions of the oxides with water.  
[treatment of peroxides and superoxides is not required]
- (h) describe and explain the acid/base behaviour of oxides and hydroxides including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids.
- (i) describe and explain the reactions of the chlorides with water.
- (j) interpret the variations and trends in (f), (g), (h), and (i) in terms of bonding and electronegativity.
- (k) suggest the types of chemical bonding present in chlorides and oxides from observations of their chemical and physical properties.
- (l) predict the characteristic properties of an element in a given group by using knowledge of chemical periodicity
- (m) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information about physical and chemical properties.

# 10.1 Periodicity in Physical Properties

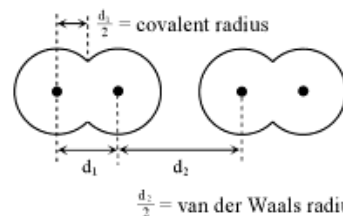
What is periodicity?

- 1) *Periodicity* is the recurrence of similar properties at regular intervals when the elements are arranged in increasing atomic number.

<i>s- block</i>				1 H		2 He		<i>p- block</i>					<i>Noble Gas</i>				
I	II											III	IV	V	VI	VII	0
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	<i>d- block</i>										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	<i>f- block</i>														
		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

## Variation in size of atoms

- 1) *Covalent radius* is half the internuclear distance between two like atoms bonded by a single covalent bond.



- 2) *Van der Waal's radius* is half the average distance between two adjacent non-bonded atoms.

- 3) For example, the covalent radius of  $\text{Cl}_2$  is 0.099 nm while the van der Waal's radius of  $\text{Cl}_2$  is 0.180 nm.

Note: van der Waal's radius is always larger than covalent radius.

- 4) *Metallic radius* is half the distance between two like metal atoms bonded by metallic bond.

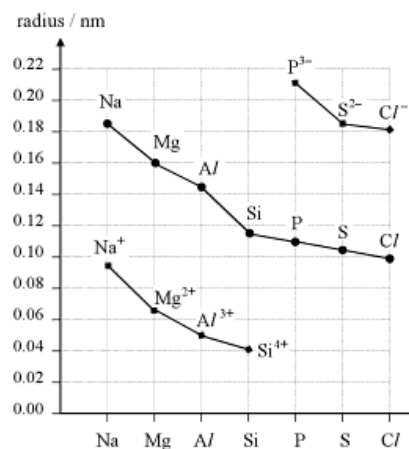
- 5) All these measurable quantities can be given a general name called 'atomic radii'.

- 6) Across Period 3, the atomic radius **decreases** gradually. This is because the **nuclear charge increases** while the **shielding effect remains constant**. The outer electrons are more attracted towards the nucleus, making the atoms smaller.
- 7) For comparison, metallic radii are used for Na, Mg and Al, covalent radii are used for Si, P, S and Cl. For argon, van der Waal's radius is used (argon do not form any bonds)

**Note:** This trend excludes argon because comparing van der Waal's radius with covalent and metallic radius is not fair.

### Variation in ionic radius

- 1) Cations are formed when an atom loses electron(s). In Period 3, Na, Mg, Al and Si form cations by losing electron(s) to achieve stable octet electronic configuration. The ions formed are  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  respectively.
- 2) Cations are **smaller** than their respective atoms because a whole layer of electrons are lost. The remaining electrons are attracted more strongly towards the centre by the same nuclear charge.

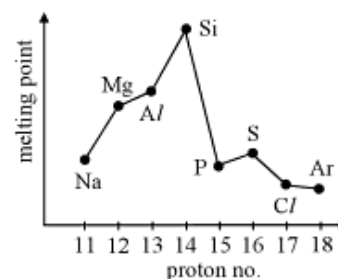


- 3) Anions are formed when an atom gains electron(s). In Period 3, P, S and Cl form anions by gaining electron(s) to achieve stable octet electronic configuration. The ions formed are  $\text{P}^{3-}$ ,  $\text{S}^{2-}$  and  $\text{Cl}^-$  respectively.
- 4) Anions are **bigger** than their respective atoms because they have more electrons than protons. The electrons are held less strongly by the nucleus. Besides, a repulsion is created between the electrons when a new electron is introduced and this causes the ion to expand.
- 5) **Anions are bigger than cations** because anions have one more shell of electrons compared to cations.
- 6) In the isoelectronic series (from  $\text{Na}^+$  to  $\text{Si}^{4+}$  and  $\text{P}^{3-}$  to  $\text{Cl}^-$ ), the ionic radius **decreases** gradually. This is because the same number of electrons are attracted more strongly by the increasing nuclear charge.

### Variation in melting and boiling points

#### 1) Across a Period,

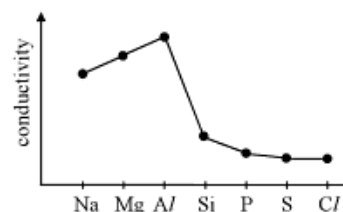
- melting point **increases from Na to Al** because the strength of the metallic bond increases.
- melting point of Si is **highest** because Si has a **giant covalent structure**, a lot of energy is required to overcome the strong covalent bonds.
- melting points of P, S, Cl and Ar are **lower** because these have **simple molecular structures**, only weak van der Waal's forces of attraction exist between them.



- 2) Melting point of  $S > P > Cl > Ar$  because these elements exist as  $S_8$ ,  $P_4$ ,  $Cl_2$  and Ar respectively.  $S_8$  contains the **most number of electrons**, followed by  $P_4$ ,  $Cl_2$  and Ar. Van der Waal's forces get stronger with increasing number of electrons.

### Variation in electrical conductivity

- 1) Across the Period, the elements change from metals (Na to Al) to semi-metal (Si) and then to non-metals (P to Ar).



- 2) Electrical conductivity is highest in metals, lower in semi-metals and lowest in non-metals (Most non-metals do not conduct electricity at all).
- 3) The electrical conductivity of Period 3 elements:
- increases from Na to Al** because the number of electrons contributed by per atom to the sea of delocalised electrons increases from one in Na, two in Mg and three in Al. There are more electrons to conduct electricity.
  - decreases from Al onwards**. Si is a semi-metal therefore it is a semi-conductor. The remaining elements do not conduct electricity because there are no mobile electrons.

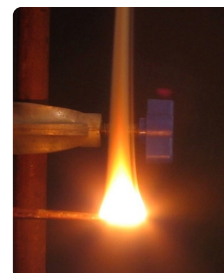
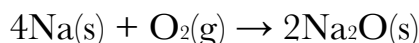
### Variation in first ionisation energy

(Refer Chapter 3)

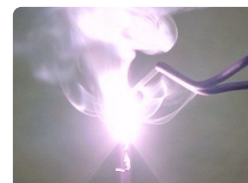
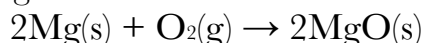
## 10.2 Periodicity in Chemical Properties

### Reaction with oxygen gas, O<sub>2</sub>

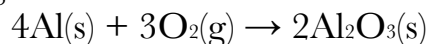
- 1) **Sodium** burns on heating with an **orange-yellow flame** to form white sodium oxide.



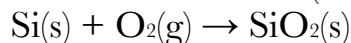
- 2) **Magnesium** burns on heating with a **brilliant white flame** to form white magnesium oxide.



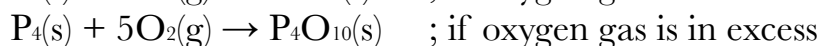
- 3) An oxide layer will form on the **aluminium** when it is exposed to air, this oxide layer prevents aluminium from reacting. However, if powdered aluminium is used, it burns on heating with **white flames** to form white aluminium oxide.



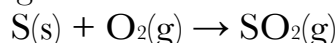
- 4) **Silicon** burns slowly at red heat to form silicon(VI) oxide or silicon dioxide.



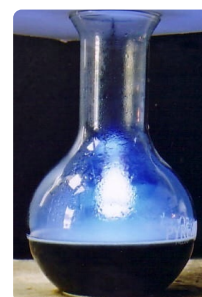
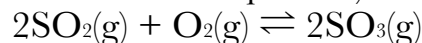
- 5) **Phosphorus** burns on heating with a **white flame** to form clouds of white covalent oxides, phosphorus(III) oxide and phosphorus(V) chloride.



- 6) **Sulfur** burns on heating with a **blue flame** to form sulfur dioxide gas.



Under suitable conditions, sulfur dioxide can be converted to sulfur trioxide. (See also the Contact process)



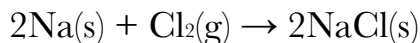
- 7) **Chlorine** forms several oxides (Cl<sub>2</sub>O and Cl<sub>2</sub>O<sub>7</sub>), but it will not react directly with oxygen.

- 8) **Argon** does not react with oxygen to form any oxides.

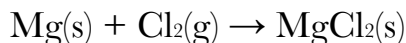
- 9) Going across Period 3, the **reactivity towards oxygen decreases** because the reducing power (tendency to be oxidised) of the elements decreases.

Reaction with chlorine gas, Cl<sub>2</sub>

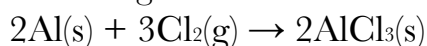
- 1) **Sodium** burns on heating in chlorine gas with an **orange-yellow flame** to form white sodium chloride.



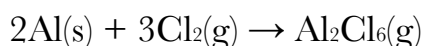
- 2) **Magnesium** burns on heating in chlorine gas with a **brilliant white flame** to form white magnesium chloride.



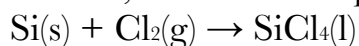
- 3) **Aluminium** burns on heating to form ionic aluminium chloride.



At temperature about 180 °C, aluminium chloride converts to a molecular form, Al<sub>2</sub>Cl<sub>6</sub>, a dimer of covalent AlCl<sub>3</sub>. At even higher temperature, Al<sub>2</sub>Cl<sub>6</sub> breaks into simple AlCl<sub>3</sub> molecules.



- 4) **Silicon** burns slowly in chlorine gas at red heat to form covalent silicon(IV) chloride or silicon tetrachloride, a colourless liquid which vaporises.

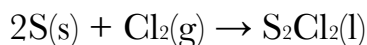


- 5) **Phosphorus** burns in chlorine gas to produce a mixture of two chlorides, phosphorus(III) chloride, PCl<sub>3</sub> and phosphorus(V) chloride, PCl<sub>5</sub>. In excess chlorine gas, PCl<sub>5</sub> is the major product.



PCl<sub>3</sub> is a fuming liquid while PCl<sub>5</sub> is an off-white solid.

- 6) **Sulfur** burns in chlorine gas to produce disulfur dichloride, an orange, evil-smelling liquid.

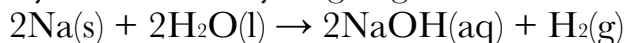


- 7) **Chlorine** obviously does not react with chlorine gas.

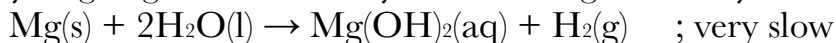
- 8) **Argon** does not react with chlorine gas to form any chlorides.

Reaction with water, H<sub>2</sub>O

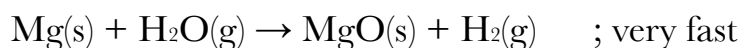
- 1) **Sodium** catches fire in cold water and a violently exothermic reaction occurs to form sodium hydroxide and hydrogen gas.



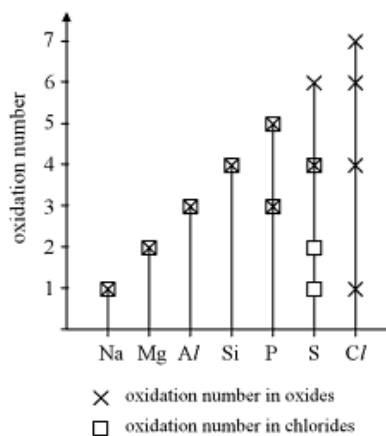
- 2) **Magnesium** reacts very slowly with cold water, taking several days to collect a test tube of hydrogen gas and a weakly alkaline magnesium hydroxide solution.



However, it reacts rapidly with steam to produce magnesium hydroxide and hydrogen gas.

Variation in oxidation number of Period 3 oxides and chlorides

- 1) Oxidation number of a Period 3 oxide or chloride corresponds to the **number of electrons used for bonding**. It is always positive because oxygen is more electronegative than any of the element.
- 2) The maximum oxidation number is the **same as Group number**. This corresponds to the total number of valence electrons.
- 3) i. In the oxides, the maximum oxidation number increases from +1 in Na to +6 in S.  
ii. In the chlorides, the maximum oxidation number increases from +1 in Na to +5 in P.
- 4) Phosphorus and sulfur show several oxidation numbers because they can expand their octet through the excitation of electrons to the empty 3d orbitals.
- 5) For example:  
i. In SO<sub>2</sub>, S has oxidation number +4 because only four electrons are used for bonding.  
ii. In SO<sub>3</sub>, S has oxidation number +6 because all six electrons are used for bonding.



## 10.3 Period 3 Oxides

Summary of the properties of Period 3 oxides.

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>6</sub> / P <sub>4</sub> O <sub>10</sub>	SO <sub>2</sub> / SO <sub>3</sub>
<i>structure</i>	<i>Ionic</i> * Al <sub>2</sub> O <sub>3</sub> is ionic with covalent character.			<i>Giant covalent</i>	<i>Simple molecular</i>	
<i>melting point</i>	<i>high</i> (strong ionic bonds must be broken for melting to occur)			<i>high</i> (strong covalent bonds must be broken)	<i>low</i> (only weak dipole-dipole forces need to be broken)	
<i>acid/base nature</i>	basic		amphoteric	(inert)	acidic	
<i>effect of water on oxide</i>	alkaline solution (pH ≈ 13)	dissolves slightly (pH ≈ 9)	Insoluble in water (high lattice energies making solution difficult)		strongly acidic solution (pH ≈ 2)	

Reaction with water, H<sub>2</sub>O

- 1) **Sodium oxide** reacts exothermically with cold water to form sodium hydroxide. A **strongly alkaline** solution of sodium hydroxide is produced.  

$$\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) \quad ; \text{pH} = 13$$
- 2) **Magnesium oxide** reacts **slightly** with water to the extent that it is almost insoluble. A **weakly alkaline** solution of magnesium hydroxide is produced.  

$$\text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{aq}) \quad ; \text{pH} = 9$$
- 3) **Aluminium oxide** does not react or dissolve in water due to its high lattice energy.
- 4) **Silicon dioxide** does not react or dissolve in water due to the strong covalent bonds.
- 5) Phosphorus oxides react with water to form **acidic solutions**(pH = 2).  
**Phosphorus(III) oxide** reacts with water to form phosphorous acid.  

$$\text{P}_4\text{O}_6(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_3(\text{aq})$$
**Phosphorus(V) oxide** reacts with water to form phosphoric(V) acid.  

$$\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq})$$
- 6) Sulfur oxides react with water to form **acidic solutions**(pH = 2).  
**Sulfur dioxide** reacts with water to give sulfurous acid or sulfuric(IV) acid.  

$$\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$$
**Sulfur trioxide** reacts violently with water to form a mist of sulfuric acid.  

$$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$$



Acid-base behaviour of Period 3 oxides

- 1) Going across Period 3, the nature of the oxide changes from **basic**( $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ) to **amphoteric**( $\text{Al}_2\text{O}_3$ ) then to **acidic**( $\text{SiO}_2$ ,  $\text{P}_4\text{O}_6/\text{P}_4\text{O}_{10}$ ,  $\text{SO}_2/\text{SO}_3$ ).  
The **acidity of the oxides increases** across the Period.
- 2) **Sodium and magnesium oxides** are **basic oxides**, they react with acid to give the corresponding **salts and water**.  

$$\text{Na}_2\text{O}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

$$\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- 3) **Aluminium oxide** is **amphoteric**, it can react with **both acid and base**.  
Aluminium oxide reacts with hot and concentrated acids to give salt and water  

$$\text{Al}_2\text{O}_3(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
  
Aluminium oxide reacts with hot and concentrated sodium hydroxide to give sodium aluminate.  

$$\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaAl}(\text{OH})_4(\text{aq})$$

sodium aluminate
- 4) **Silicon dioxide** is an **acidic oxide**, it reacts with hot and concentrated sodium hydroxide to give a colourless solution of sodium silicate.  

$$\text{SiO}_2(\text{s}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SiO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

sodium silicate
- 5) Phosphorus oxides are **acidic oxides**, they react with alkalis to form salts and water.  
**Phosphorus(III) oxide** reacts with sodium hydroxide to form sodium phosphate(III) and water.  

$$\text{P}_4\text{O}_6(\text{s}) + 12\text{NaOH}(\text{aq}) \rightarrow 4\text{Na}_3\text{PO}_3(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$$
  
**Phosphorus(V) oxide** reacts with sodium hydroxide to form sodium phosphate(V) and water.  

$$\text{P}_4\text{O}_{10}(\text{s}) + 12\text{NaOH}(\text{aq}) \rightarrow 4\text{Na}_3\text{PO}_4(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$$
- 6) Sulfur oxides are **acidic oxides**, they react with alkalis to form salt and water.  
**Sulfur dioxide** reacts with sodium hydroxide to form sodium sulfate(IV) and water.  

$$\text{SO}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
  
**Sulfur trioxide** reacts with sodium hydroxide to form sodium sulfate(VI) and water.  

$$\text{SO}_3(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

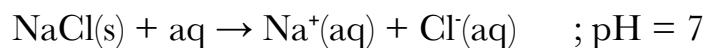
## 10.4 Period 3 Chlorides

### Summary of the properties of Period 3 chlorides

	NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>	PCl <sub>3</sub> /PCl <sub>5</sub>
<i>structure</i>	<i>Giant ionic</i> (composed of oppositely charged ions held together by strong electrostatic forces)		<i>Simple molecular</i> (composed of small discrete molecules held together by weak van der Waals' forces)		
<i>melting point</i>	<i>high</i> (strong ionic bonds must be broken for melting to occur)		<i>sublimes #</i> (at 180 °C)	<i>low</i> (only weak van der Waals' forces need to be broken) * <i>Exception: PCl<sub>3</sub> solid</i>	
<i>effect of water on chloride</i>	dissolve readily (neutral solution) (pH ≈ 7)		hydrolyse to give fumes of HCl gas; acidic solution (pH ≈ 3)		

### Reaction with water, H<sub>2</sub>O

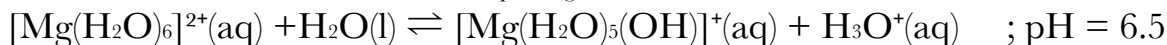
- 1) **Sodium chloride** dissolves in water to form a **neutral solution** of sodium chloride.



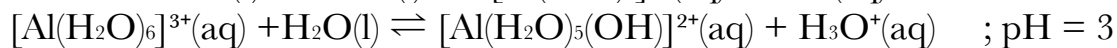
- 2) **Magnesium chloride** dissolves in water with slight hydrolysis to form a solution of magnesium chloride.



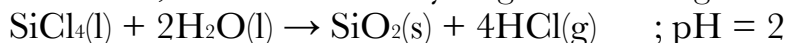
hexaaquamagnesium ions



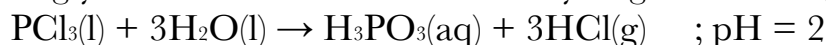
- 3) **Aluminium chloride**, AlCl<sub>3</sub> hydrolyses in water to give an acidic solution, white fumes of hydrogen chloride gas are formed.



- 4) **Silicon tetrachloride** undergoes complete hydrolysis in water to form a strongly acidic solution, white fumes of hydrogen chloride gas are formed.



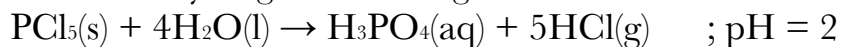
- 5) **Phosphorus(III) chloride** reacts violently with water in a hydrolysis reaction to give a strongly acidic solution and fumes of hydrogen chloride gas.



**Phosphorus(V) chloride** is an off-white ionic solid at room temperature and sublimates at 163 °C to give phosphorus(III) chloride and chlorine gas.



It reacts violently with water in a hydrolysis reaction to give a strongly acidic solution and fumes of hydrogen chloride gas.



- 6) The **acidity of the chlorides increases** across the Period as the nature of the chlorides changes from ionic to covalent.