PERIODICITY

The oxides of period 3 elements
The chlorides of period 3 elements
The reaction of period 3 elements with water

Students should be able to show the variation in properties across Period 3 (sodium to argon) as illustrated by:

(i) reactions of the elements with oxygen, chlorine and water

(ii) the formulae and acid-base character of the oxides and hydroxides of the metals and oxides of the non-metals
limited to Na_2O, MgO, Al_2O_3, $NaOH$, $Mg(OH)_2$, $Al(OH)_3$, SiO_2, P_4O_{10}, SO_2, SO_3 *and* Cl_2O

(iii) the formulae of the chlorides, and their reactions with water
the reaction with water limited to $NaCl$, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_3, PCl_5, S_2Cl_2

(iv) interpret the reactions in (a)(ii) and (a)(iii) in terms of the structure and bonding of the oxides and chlorides

THE OXIDES OF PERIOD 3 ELEMENTS

1. Formation of oxides

All the elements in Period 3 except chlorine and argon combine directly with oxygen to form oxides.

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$
Na_2O is an ionic oxide.

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
MgO is also an ionic oxide.

$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$
Al_2O_3 is mostly ionic, but there is significant covalent character.

$Si(s) + O_2(g) \rightarrow SiO_2(s)$
SiO_2 is a giant covalent oxide.

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$
P_4O_{10} is a molecular covalent oxide. The oxidation number of P in this oxide is +5.

$S(s) + O_2(g) \rightarrow SO_2(g)$
SO_2 is a molecular covalent oxide.

Another oxide, SO_3 is formed in a reversible process when SO_2 and O_2 are heated with a V_2O_5 catalyst (the Contact Process)

2. Physical properties of oxides

The physical properties of these oxides depend on the type of bonding.

Na_2O, Al_2O_3 and MgO are ionic oxides and hence have a high melting point. MgO and Al_2O_3 have a higher melting point than Na_2O since the charges are higher, resulting in a stronger electrostatic forces of attraction between the ions.

SiO_2 has a giant covalent structure and hence a high melting point. There are strong covalent bonds between all the atoms and thus lots of energy is required to break them.

P_4O_{10} and SO_3 are molecular covalent and so only intermolecular forces(Van der Waal's forces) exist between the molecules. The melting points are thus much lower. P_4O_{10} has a higher molecular mass than SO_3 and so has a much higher melting point, as the van der Waal's forces are stronger.

Element	Na	Mg	Al	Si	P	S

Formulae of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3
Structure of oxide	Ionic	Ionic	Mostly ionic	Giant covalent	Molecular covalent	Molecular covalent
Melting point of oxide /°C	1275	2852	2072	1703	300	-10

3. **Acid-base character of oxides**

Ionic oxides contain the O^{2-} ion. This is a strongly basic ion which reacts with water to produce hydroxide ions:

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

Thus all ionic oxides are BASIC.

Covalent oxides do not contain ions, but have a strongly positive dipole on the atom which is not oxygen. This attracts the lone pair of electrons on water molecules, releasing H^+ ions:

$$XO(s) + H_2O(l) \rightarrow XO(OH)^-(aq) + H^+(aq)$$

Thus all covalent oxides are ACIDIC.

Intermediate oxides can react in either of the above ways, depending on the conditions. They can thus behave as either acids or bases and are thus AMPHOTERIC.

Na_2O is a basic oxide. It dissolves in water to give an alkaline solution (pH = 14). It also reacts with acids to form a salt and water:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

$$Na_2O(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2O(l)$$

MgO is a basic oxide. It is only slightly soluble in water and so the solution is only slightly alkaline (pH = 9). It also reacts readily with acids:

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$$
$$MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$$

Al_2O_3 is an amphoteric oxide. It is insoluble in water (pH = 7) but dissolves in both acids and alkalis:

$$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$$
$$Al_2O_3(s) + 3H_2O(l) + 6OH^-(aq) \rightarrow 2Al(OH)_6^{3-}(aq)$$

$$Al_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq)$$

SiO_2 is an acidic oxide. It is insoluble in water (pH = 7) but dissolves in hot concentrated alkalis:

$$SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$$

P_4O_{10} is an acidic oxide. It dissolves in water to give acidic solutions and is also soluble in alkalis(since it is acidic):

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq) \qquad pH = 3$$
$$P_4O_{10}(s) + 12OH^-(aq) \rightarrow 4PO_4^{3-}(aq) + 6H_2O(l)$$

SO_2 and SO_3 are acidic oxides. They dissolve in water to give acidic solutions, and also react with alkalis:

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq), \quad pH = 2$$
$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq), \quad pH = 1$$
$$SO_2(g) + 2OH^-(aq) \rightarrow SO_3^{2-}(aq) + H_2O(l)$$
$$SO_3(g) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l)$$

SO_2 is a waste gas in many industrial processes. It is harmful because it dissolves in rain water to give acid rain. It can be removed from waste gases because it dissolves in alkali and so it is passed through an alkaline solution in waste gas outlets to minimise the amount which escapes into the atmosphere.

The acid-base properties of the oxides of Period 3 can be summarised in the following table:

Element	Na	Mg	Al	Si	P	S
Formulae of oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2 SO_3
Acid-base character of oxide	Basic	Basic	Amphoteric	Acidic	Acidic	Acidic
pH of solution when dissolved in water	12 - 14	8 - 9	7 (insoluble)	7 (insoluble)	2 - 4	2 - 4 (SO_2) 1 - 3 (SO_3)

The oxides therefore become more acidic on moving from left to right in the periodic table.

THE CHLORIDES OF PERIOD 3 ELEMENTS

4. **Formation of chlorides**

All the elements of Period 3 except argon combine directly with chlorine to give chlorides.

$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
NaCl is an ionic chloride.

$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
$MgCl_2$ is also an ionic chloride.

$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$
$AlCl_3$ is covalent. It forms a polymeric structure in the solid state, turning quickly on heating into a dimeric gas (Al_2Cl_6). It thus behaves as a simple molecular chloride.

$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(s)$
$SiCl_4$ is a molecular covalent chloride.

$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(s)$
PCl_5 is formed by reacting PCl_3 with excess chlorine in a reversible reaction:
$PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)$

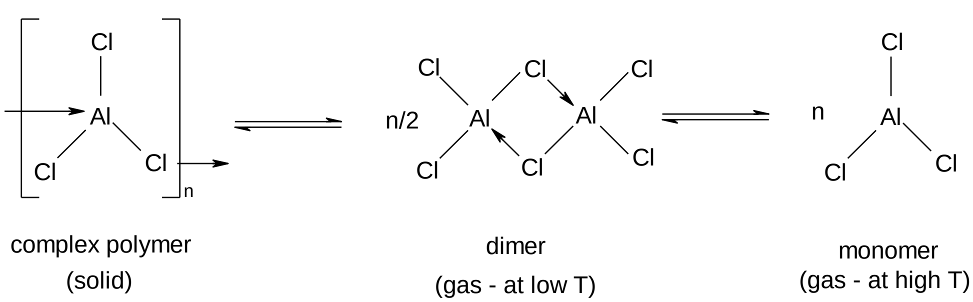
PCl_5 is actually ionic in the solid state - it exists as $[PCl_4]^+[PCl_6]^-$ in the solid state.

5. **Physical properties of chlorides**

NaCl and $MgCl_2$ are ionic chlorides. Since a large amount of energy is required to separate the ions, the melting point is high.

$AlCl_3$ and $SiCl_4$ are molecular covalent chlorides, and so only intermolecular forces exist between the molecules. The melting points are thus much lower than the ionic chlorides.

$AlCl_3$ actually exists in polymeric form in the solid state, which is converted to a dimeric form in the gas phase. At high temperatures, it reverts to a simple molecular structure:



The aluminium atom is electron deficient – it has only 3 of its four valence orbitals occupied, so it has an empty orbital with which it can accept a lone pair of electrons from a Cl atom on an adjacent monomer.

PCl_5 is ionic so its melting point is thus high. On heating, however, it reverts to a simple covalent structure and sublimes.

Element	Na	Mg	Al	Si	P
Formula of chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
Structure of chloride	ionic	ionic	polymer	molecular covalent	Ionic
Melting point of chloride /°C	801	710	184	58	162

6. **Reaction of chlorides with water**

The way in which chlorides react with water depends on the type of bonding present in the chloride:

Ionic chlorides dissolve in water and only dissociate to give neutral solutions:

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ pH = 7

$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ pH = 7

Aluminium chloride reacts with water to give hydrated aluminium ions and chloride ions. The hydrated aluminium ions undergo deprotonation (hydrolysis) to give an acidic solution:

$AlCl_3(s) + 6H_2O(l) \rightarrow Al(H_2O)_6^{3+}(aq) + 3Cl^-(aq)$

$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightarrow [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

The other covalent chlorides react readily with water at room temperature to form the oxide or hydroxide and HCl(g). The HCl is formed as white misty fumes, and the observance of these fumes is a good indication that the chloride is covalent.

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$ pH = 1 – 2

$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g)$ pH = 1 - 2

Covalent chlorides thus react with water to give acidic solutions. The acidity is due to dissolved HCl.

The water molecules attack the covalent chlorides by donating lone pairs of electrons into empty low-lying orbitals on the electropositive atoms. In the case of $AlCl_3$, there is an available 3p orbital, and in $SiCl_4$ and PCl_5 there are available d-orbitals

		3s	3p			3d				
$AlCl_3$	[Ne]	↓↑	↓↑	↓↑						
$SiCl_4$	[Ne]	↓↑	↓↑	↓↑	↓↑					
PCl_5	[Ne]	↓↑	↓↑	↓↑	↓↑	↓↑				

It the availability of these low-lying empty orbitals which enables these chlorides to react readily with water.

THE REACTION OF PERIOD 3 ELEMENTS WITH WATER

Na, Mg, Al and Si are more electropositive than H and can reduce the water to hydrogen gas:

Na reacts vigorously with water to give the hydroxide and hydrogen:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

The resulting solution is strongly alkaline, and will have a pH of 14.

Mg reacts with steam to give the oxide and hydrogen:

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

The resulting solution is weakly alkaline, since the oxide is slightly basic (pH = 9).

Al and Si also react with steam under certain conditions.

P, S and Cl_2 do not reduce water to hydrogen gas. Phosphorus and sulphur do not react with water but chlorine will disproportionate to give an acidic solution:

$$Cl_2(g) + H_2O(l) \rightarrow HClO(aq) + HCl(aq)$$

The resulting solution contains HCl(aq) and is thus acidic (pH = 2).

The reactivity of the elements of period 3 towards water thus decreases from Na to Si, and then increases from P to Cl. The resulting solutions become increasingly acidic.