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 Na_2O, MgO, Al_2O_3, P_4O_{10}, SO_2, SO_3), chlorine (to give $NaCl$, $MgCl_2$, Al_2Cl_6, $SiCl_4$, 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.

s- block | d- block | p- block | Noble Gas

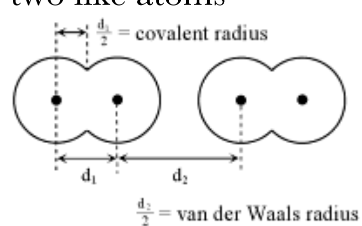
I	II											III	IV	V	VI	VII	0
				1 H	2 He												
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	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															

f- block

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 Cl_2 is 0.099 nm while the van der Waal's radius of Cl_2 is 0.180 nm.
Note: van der Waal's radius is always larger than covalent radius.

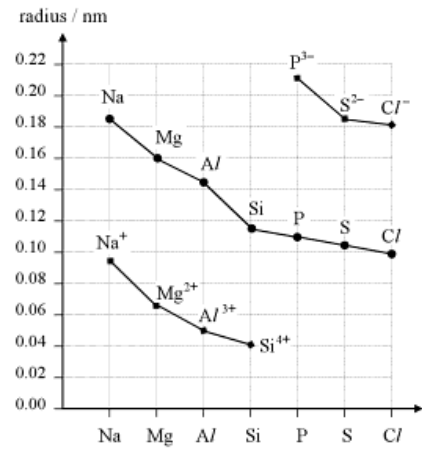
4) *Metallic radius* is half the distance between two like metal atoms bonded by metallic bond.

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 Na^+, Mg^{2+}, Al^{3+} and 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.

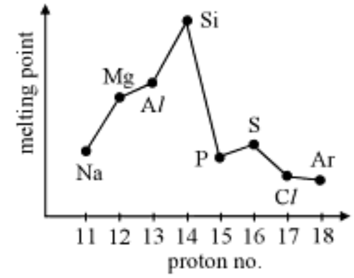
3) Anions are formed when an atom gains electron(s). In Period 3, P, S and Cl form anions by gaining electron(s) to achieve stable octet electronic configuration. The ions formed are P^{3-}, S^{2-} and Cl^- respectively.

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 Na^+ to Si^{4+} and P^{3-} to Cl^-), the ionic radius **decreases** gradually. This is because the same number of electrons are attracted more strongly by the increasing nuclear charge.

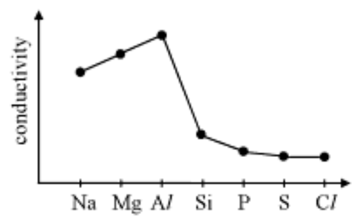
Variation in melting and boiling points



1) Across a Period,
   i. melting point **increases from Na to Al** because the strength of the metallic bond increases.
   ii. 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.
   iii. 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 is 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:
   i. **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.
   ii. **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 is first ionisation energy

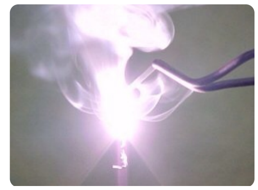
(Refer Chapter 3)

10.2 Periodicity in Chemical Properties

Reaction with oxygen gas, O_2

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

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$



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

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

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.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

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

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$

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

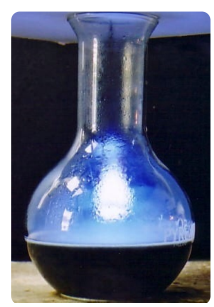
$$P_4(s) + 3O_2(g) \rightarrow P_4O_6(s) \quad \text{; if oxygen gas is limited}$$
$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \text{; if oxygen gas is in excess}$$

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

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

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

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$



7) **Chlorine** forms several oxides(Cl_2O and Cl_2O_7), 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_2

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

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

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

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

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

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

At temperature about 180 °C, aluminium chloride converts to a molecular form, Al_2Cl_6, a dimer of covalent $AlCl_3$. At even higher temperature, Al_2Cl_6 breaks into simple $AlCl_3$ molecules.

$$2Al(s) + 3Cl_2(g) \rightarrow Al_2Cl_6(g)$$

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

$$Si(s) + Cl_2(g) \rightarrow SiCl_4(l)$$

5) **Phosphorus** burns in chlorine gas to produce a mixture of two chlorides, phosphorus(III) chloride, PCl_3 and phosphorus(V) chloride, PCl_5. In excess chlorine gas, PCl_5 is the major product.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l) \qquad \text{; if chlorine gas is limited}$$

$$P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(s) \qquad \text{; if chlorine gas is in excess}$$

PCl_3 is a fuming liquid while PCl_5 is an off-white solid.

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

$$2S(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$$

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_2O

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

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

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.

$$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g) \quad \text{; very slow}$$

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

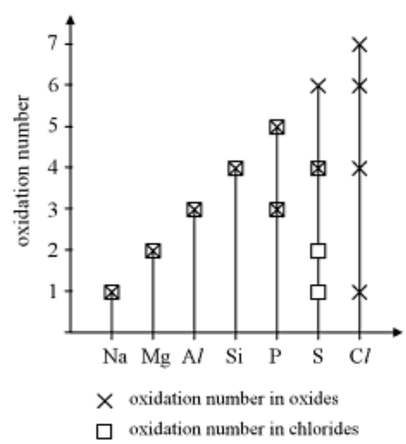
$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g) \quad \text{; very fast}$$

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_2, S has oxidation number +4 because only four electrons are used for bonding.
   ii. In SO_3, 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_2O	MgO	Al_2O_3	SiO_2	P_4O_6 / P_4O_{10}	SO_2 / SO_3
structure	*Ionic* * Al_2O_3 is ionic with covalent character.			*Giant covalent*	*Simple molecular*	
melting point	*high* (strong ionic bonds must be broken for melting to occur)			*high* (strong covalent bonds must be broken)	*low* (only weak dipole-dipole forces need to be broken)	
acid/base nature	basic		amphoteric	(inert)	acidic	
effect of water on oxide	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_2O

1) **Sodium oxide** reacts exothermically with cold water to form sodium hydroxide. A **strongly alkaline** solution of sodium hydroxide is produced.
$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq) \quad ; pH = 13$$

2) **Magnesium oxide** reacts **slightly** with water to the extent that it is almost insoluble. A **weakly alkaline** solution of magnesium hydroxide is produced.
$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq) \quad ; pH = 9$$

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.
$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$
Phosphorus(V) oxide reacts with water to form phosphoric(V) acid.
$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

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.
$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$
Sulfur trioxide reacts violently with water to form a mist of sulfuric acid.
$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Acid-base behaviour of Period 3 oxides

1) Going across Period 3, the nature of the oxide changes from **basic(Na_2O, MgO)** to **amphoteric(Al_2O_3)** then to **acidic(SiO_2, P_4O_6/P_4O_{10}, SO_2/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**.

$$Na_2O(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l)$$
$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

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

$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

Aluminium oxide reacts with hot and concentrated sodium hydroxide to give sodium aluminate.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow \underset{\text{sodium aluminate}}{2NaAl(OH)_4(aq)}$$

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

$$SiO_2(s) + 2NaOH(aq) \rightarrow \underset{\text{sodium silicate}}{Na_2SiO_3(aq)} + H_2O(l)$$

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.

$$P_4O_6(s) + 12NaOH(aq) \rightarrow 4Na_3PO_3(aq) + 6H_2O(l)$$

Phosphorus(V) oxide reacts with sodium hydroxide to form sodium phosphate(V) and water.

$$P_4O_{10}(s) + 12NaOH(aq) \rightarrow 4Na_3PO_4(aq) + 6H_2O(l)$$

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.

$$SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$$

Sulfur trioxide reacts with sodium hydroxide to form sodium sulfate(VI) and water.

$$SO_3(g) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$

10.4 Period 3 Chlorides

Summary of the properties of Period 3 chlorides

	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3/PCl_5
structure	*Giant ionic* (composed of oppositely charged ions held together by strong electrostatic forces)		*Simple molecular* (composed of small discrete molecules held together by weak van der Waals' forces)		
melting point	*high* (strong ionic bonds must be broken for melting to occur)		*sublimes* # (at 180 °C)	*low* (only weak van der Waals' forces need to be broken) * *Exception*: PCl_5 solid	
effect of water on chloride	dissolve readily (neutral solution) (pH ≈ 7)	(slightly acidic) (pH ≈ 6.5)	hydrolyse to give fumes of HCl gas; acidic solution (pH ≈ 3)	(pH ≈ 2)	

Reaction with water, H_2O

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

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

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

$$MgCl_2(s) + 6H_2O \rightarrow \underbrace{[Mg(H_2O)_6]^{2+}(aq)}_{\text{hexaaquamagnesium ions}} + 2Cl^-(aq)$$

$$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq) \qquad ; pH = 6.5$$

3) **Aluminium chloride**, $AlCl_3$ hydrolyses in water to give an acidic solution, white fumes of hydrogen chloride gas are formed.

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

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq) \qquad ; pH = 3$$

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

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

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

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(g) \qquad ; pH = 2$$

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

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

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

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

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