

2022 JC1 H2 CHEMISTRY (9729) CORE IDEA 2 – STRUCTURES AND PROPERTIES Topic 11: THE PERIODIC TABLE

Name:	Civics Group:
Name.	 Civics Group.

Trends and variations in atomic and physical properties

For elements in the third period (sodium to chlorine), and in Group 2 (magnesium to barium) and Group 17 (chlorine to iodine) candidates should be able to:

- (a) recognise variation in the electronic configurations across a Period and down a Group
- (b) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity:
 - (i) across a Period in terms of shielding and nuclear charge
 - (ii) down a Group in terms of increasing number of electronic shells and nuclear charge
- interpret the variation in melting point and in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular)
- (d) describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction

Trends and variations in chemical properties

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

- (e) (i) state and explain the variation in the highest oxidation number of the elements in oxides (for Na₂O; MgO; Al₂O₃; SiO₂; P₄O₁₀; SO₃) and chlorides (for NaCl; MgCl₂; AlCl₃; SiCl₄; PCl₅)
 - (ii) state and explain the variation in bonding in oxides and chlorides in terms of electronegativity (with the exception of AICI₃)
 - (iii) describe the reactions of the oxides with water (for Na₂O; MgO; Al₂O₃; SiO₂; P₄O₁₀; SO₃)
 - (iv) describe and explain the acid/base behaviour of oxides (for Na₂O; MgO; Al₂O₃; SiO₂; P₄O₁₀; SO₃) and hydroxides (for NaOH; Mg(OH)₂; Al(OH)₃), including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids
 - (v) describe and explain the reactions of the chlorides with water (for NaC1; MgC12; A1C13; SiC14; PC15)
 - (vi) suggest the types of structure and bonding present in the oxides and chlorides from observations of their chemical and physical properties

For elements in Group 2 (magnesium to barium) and Group 17 (chlorine to iodine) candidates should be able to:

- (f) describe and deduce from E^{\oplus} values the relative reactivity of elements of:
 - (i) Group 2 as reducing agents
 - (ii) Group 17 as oxidising agents
- (g) describe and explain the trend in thermal stability of:
 - (i) Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion
 - (ii) Group 17 hydrides in terms of bond energies

In addition, candidates should be able to:

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

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REFERENCES

1 Chemistry (for CIE AS & A Level) by Peter Cann & Peter Hughes

1 Introduction (INDEPENDENT STUDY)

The Periodic Table is an arrangement of elements in order of **increasing atomic (proton) number**. The properties of the elements are a periodic function of their atomic numbers (*i.e.* repeating after a regular interval).

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s bl	lock		d block										p bl	ock			
Period																		
1								Н										Не
2	Li	Ве											В	С	N	0	F	Ne
3	Na	Mg	+			Trai	nsitio	n me	etals			-	Αl	Si	Р	S	Cl	Ar
4	K	Ca	Sc	Ti	٧	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Υ	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
6	Cs	Ва	lanthanoids	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Τl	Pb	Bi	Ро	At	Rn
7	Fr	Ra	actinoids	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Fl		Lv		

Block	Electronic Configuration
s block	ns¹ to ns²
p block	ns ² np ¹ to ns ² np ⁶
	[Ar] 3d ¹ 4s ² to [Ar] 3d ¹⁰ 4s ²
d block	[Kr] 4d ¹ 5s ² to [Kr] 4d ¹⁰ 5s ²
a block	[Xe] 4f ¹⁴ 5d ² 6s ² to [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²
	[Rn] 5f ¹⁴ 5d ² 6s ² to [Rn] 5f ¹⁴ 5d ¹⁰ 6s ²
f block	[Xe] 5d ¹ 6s ² to [Xe] 4f ¹⁴ 5d ¹ 6s ²
/ DIOCK	[Rn] 6d ¹ 7s ² to [Rn] 5f ¹⁴ 6d ¹ 7s ²

Note: electronic configurations stated for the s and p block are *valence* electronic configurations.

		f block													
lanthanoids	La	Се	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
actinoids	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

<u>Group</u>

- Refers to the vertical columns of elements in the Periodic Table.
- Elements within the same Group have the same outer electronic configuration and hence similar chemical properties.

Period

- Refers to the horizontal rows of elements in the Periodic Table.
- * Period number = Number of electron shells (or Principal Quantum Shells)
- Elements within the same Period have the same number of electron shells.

Periodicity

* Refers to the recurrence of similar properties at regular intervals when elements are arranged in increasing atomic number.

2 Trend and Properties of Period 3 Elements (INDEPENDENT STUDY)

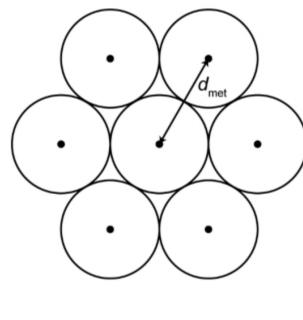
- LO (a) recognise variation in the electronic configurations across a Period and down a Group
 - (b) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity:
 - (i) across a Period in terms of shielding and nuclear charge
 - (ii) down a Group in terms of increasing number of electronic shells and nuclear charge
 - (c) interpret the variation in melting point and in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular)

2.1 Atomic Radius

Atomic radius is defined as half the distance between the centres of two adjacent atoms found in the structure of the element.

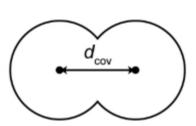
It can be measured differently, depending on the inter-atomic bonding:

The metallic radius of an atom is half the distance between the centres of two adjacent atoms in the metal



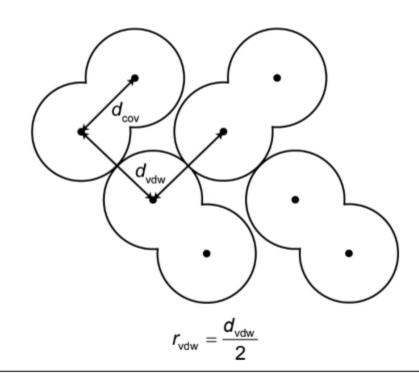
 $r_{\text{met}} = \frac{d_{\text{met}}}{2}$

The covalent radius of an atom is half the distance between the centres of two adjacent atoms that are covalently bonded e.g. within Cl₂ molecules



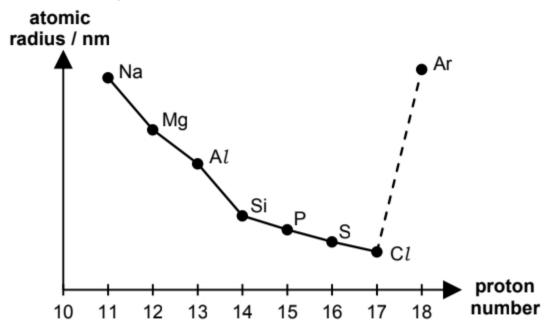
$$r_{cov} = \frac{d_{cov}}{2}$$

* The van der Waals' radius of an atom is half the distance between the centres of two adjacent atoms which are not chemically bonded e.g. between Cl₂ molecules in solid Cl₂



For example, for Cl₂ molecules, we can consider its covalent radius (0.102 nm) and van der Waals' radius (0.175 nm). For noble gases such as argon, however, as it does not form any compounds, we will only consider its van der Waals' radius (0.190 nm). **To make meaningful comparisons between the sizes of different atoms, we will usually compare the radii of the same type**.

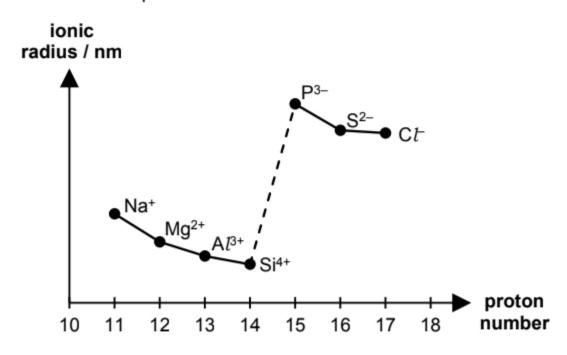
Graph 1: Trend of Atomic Radii Across Period 3



Period 3 element	Na	Mg	Αl	Si	Р	s	C1	Ar
Atomic No.	11	12	13	14	15	16	17	18
Electronic Configuration	[Ne] 3s ¹	[Ne] 3s ²	[Ne] 3s ² 3p ¹	[Ne] 3s ² 3p ²	[Ne] 3s ² 3p ³	[Ne] 3s ² 3p ⁴	[Ne] 3s ² 3p ⁵	[Ne] 3s ² 3p ⁶
Atomic Radius	 Number of property Same number Increase in experiments 	er of inner shell ele	us of the atom inc ectrons, thus <u>shiel</u> <u>charge</u>	reases, thus nucle ding effect is app etween the nucleu	proximately cons	<u>tant</u>		* r _{Ar} appears to be the largest as value (0.190 nm) in <i>Data Booklet</i> is the van der Waals' radius.

2.2 Ionic Radius

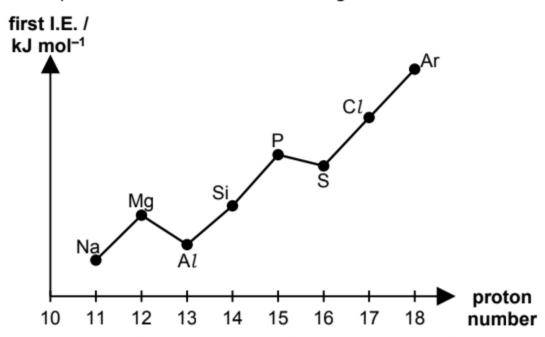
Graph 2: Trend of Ionic Radii Across Period 3



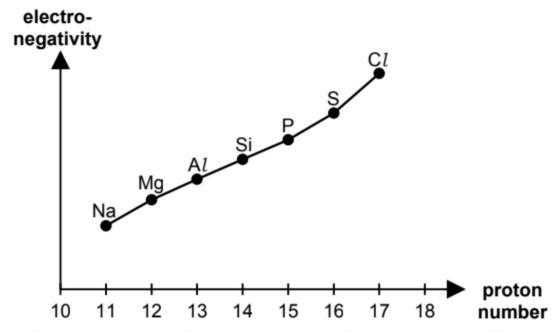
Period 3 element	Na	Mg	A!	Si	Р	s	CI	Ar
Atomic No.	11	12	13	14	15	16	17	18
Period 3 ions	11 Na ⁺	₁₂ Mg ²⁺	13 A l^{3+}	14Si ⁴⁺	₁₅ P ³ –	16 S ²⁻	17 C <i>l</i>	
Electronic Configuration	[He] 2s ² 2p ⁶	[He] 2s ² 2p ⁶	[He] 2s ² 2p ⁶	[He] 2s ² 2p ⁶	[Ne] 3s ² 3p ⁶	[Ne] 3s ² 3p ⁶	[Ne] 3s ² 3p ⁶	
Ionic Radius	Nuclear charge Same inter-ele (same number Stronger elect valence electro Size of anions > Anions have o	ectronic repulsion of electrons) trostatic forces of at	since the cations traction between the cipal quantum sho	e nucleus and the	Nuclear charge Same inter-ele isoelectronic (s Stronger elect the nucleus an	e increases ectronic repulsion si same number of ele trostatic forces of a d the valence elect	nce the anions are ectrons) attraction between	
		ostatic forces of attr				ns than in cations		

2.3 1st Ionisation Energy and Electronegativity

Graph 3: Trend of 1st Ionisation Energies Across Period 3



Graph 4: Trend of Electronegativities Across Period 3



Period 3 element	Na	Mg	Al	Si	Р	s	Cl	Ar
Atomic No.	11	12	13	14	15	16	17	18
Electronic Configuration	[Ne] 3s ¹	[Ne] 3s ²	[Ne] 3s ² 3p ¹	[Ne] 3s ² 3p ²	[Ne] 3s ² 3p ³	[Ne] 3s ² 3p ⁴	[Ne] 3s ² 3p ⁵	[Ne] 3s ² 3p ⁶

Across the period, 1st IE generally increase because:

- Number of protons in the nucleus of the atom increases, thus nuclear charge increases
- Same number of inner shell electrons, thus shielding effect is approximately constant
- Increase in effective nuclear charge
- * Increase in electrostatic forces of attraction between the nucleus and valence electron
- More energy needed to remove the valence electron, increase in 1st I.E. across the period

1st Ionisation Energy

1st IE of Al is lower than Mg because:

- The 3p electron to be removed from Al is at a higher energy level than the 3s electron to be removed from Mg.
- Less energy is required to remove the 3p electron from Al.

1st IE of S is lower than P because:

- * There is inter-electronic repulsion between the paired electrons in the same orbital for S.
- * Less energy is thus required to remove a 3p electron from S due to inter-electron repulsion between the paired electrons in the same orbital.

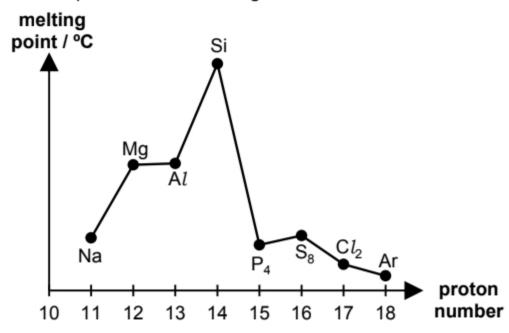
Electronegativity

Across the period, electronegativity increases because:

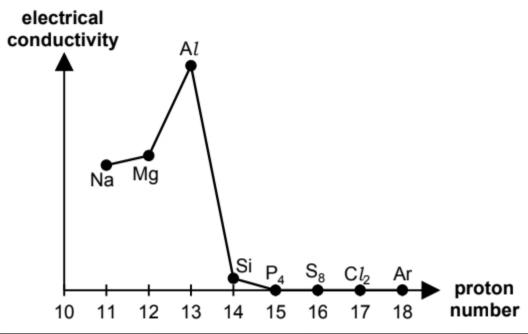
- Number of protons in the nucleus of the atom increases, thus <u>nuclear charge increases</u>
- Same number of inner shell electrons, thus shielding effect is approximately constant, increase in effective nuclear charge
- * Increase in electrostatic forces of attraction between the nucleus and valence electron

2.4 Melting Point and Electrical Conductivity

Graph 5: Trend of Melting Points Across Period 3



Graph 6: Trend of Electrical Conductivities Across Period 3



Period 3 element	Na	Mg	Al	Si	P (P ₄)	S (S ₈)	C1 (C12)	Ar		
					P.P.	S S S S	cl—cl			
Structure	Giant	metallic lattice str	ucture	Giant molecular		Simple molec	cular structure			
Melting Point	Melting points of Melting poin	t of energy is need etallic bonds. of Al > Mg > Na be maked tributed per atom	cause: ed valence rcome the strong on between metal	High melting point because: ** Large amount of energy is needed to overcome the strong and extensive covalent bonds between atoms	intermolecularing interactions Melting points of increase in name increase in part in part in part increase in part in	ints because: t of energy is need ar instantaneous of S ₈ > P ₄ > C l ₂ > A umber of electron olarisability of ele required to overcor is dipole-induced	dipole-induced d Ar because: as in the molecule ectron cloud me stronger interi	ipole molecular		
Electrical Conductivity	▶ Presence of s	conductivity because of delocalised e carriers to condu	electrons as	Low electrical conductivity because: * Si is a metalloid.	Non-conductors of electricity in any state because: Electrons are localised in covalent bonds and not mobile to conduct electricity.					

3 Trend and Properties of Period 3 Oxides and Chlorides

3.1 Oxidation numbers

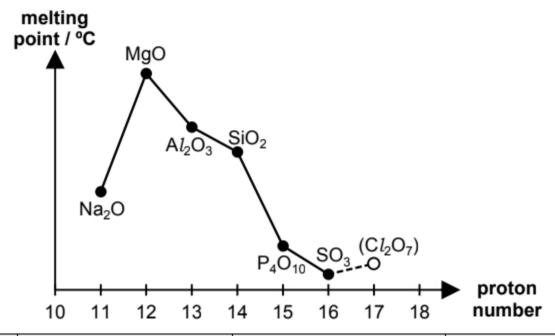
LO (d) (i) state and explain the variation in the highest oxidation number of the elements in oxides (for Na₂O; MgO; Al₂O₃; SiO₂; P₄O₁₀; SO₃) and chlorides (for NaCl; MgCl₂; AlCl₃; SiCl₄; PCl₅)

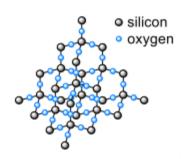
Period 3 element	Na	Mg	A1	Si	Р	s
Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	(P ₄ O ₆) P ₄ O ₁₀	(SO ₂) SO ₃
Chloride	NaC1	MgC1 ₂	AlCl ₃	SiC14	(PC <i>l</i> ₃) PC <i>l</i> ₅	
	+1	+2	+3	+4	(+3) +5	(+4) +6
Oxidation number	Number of valence el Maximum oxidation n	ectrons available for bond umber = number of valend	formation increases. ce electrons of an atom			
				be used for bonding thro	ugh expansion of the oc	tet structure.

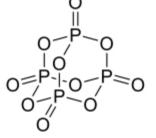
3.2 Melting Points

- LO (d) (i) state and explain the variation in bonding in oxides and chlorides in terms of electronegativity (with the exception of A/C/₃)
 - (vi) suggest the types of structure and bonding present in the oxides and chlorides from observations of their chemical and physical properties

Graph 7: Trend of Melting Points of Period 3 Oxides

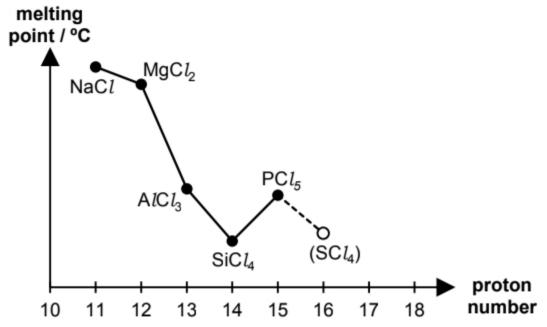






Period 3 oxide	Na₂O	MgO	A l₂O₃	SiO ₂	P ₄ O ₁₀	SO₃
Structure		Giant ionic structure		Giant molecular	Simple moled	cular structure
Melting point of oxides	Melting points of MgO ΔH _{latt} ∞ q ⁺ × q ⁻ / r ₊ + r ₋ Anionic charge and a ionic charge and small	rgy is needed to overcome Na2O because: nionic radius remain the second radius than Noted to overcome the strong A l2O3 because: charge and smaller ion	nger ionic bonds in MgO. nic radius than Mg ²⁺ higher polarising power	High melting point because: ** Large amount of energy is needed to overcome the strong and extensive covalent bonds between atoms	 Increase in polarisa cloud More energy require 	ergy is needed to intermolecular ole-induced dipole 0 > SO ₃ because: 04O ₁₀ molecule than SO ₃ ability of electron ed to overcome cular_instantaneous

Graph 8: Trend of Melting Points of Period 3 Chlorides

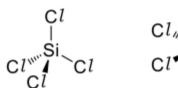


FYI: More information about AIC 13

- At temperatures above 180 °C, the chloride exists as a molecular dimer, A l₂C l₆ held together by instantaneous dipole-induced dipole attraction.
- * The dimer persists in the gaseous phase when the liquid boils:

$$Al_2Cl_6(l) \stackrel{\text{heat}}{=\!=\!=\!=} Al_2Cl_6(g)$$

At higher temperatures, gaseous Al₂Cl₆ dissociates to give monomeric AlCl₃ molecules:

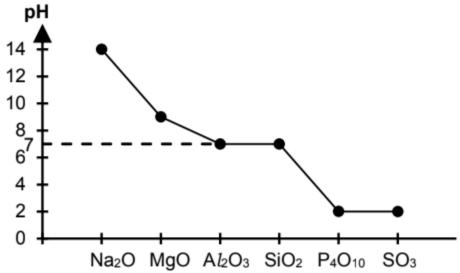


Period 3 chloride	NaC1	MgC ℓ₂	AIC1 ₃	SiC4	PC <i>1</i> ₅				
			Simple molecular structure						
			A l³+ has high ionic charge and small ionic radius						
Structure	Giant ionic	structure	A R ³⁺ has a high charge density and hence high polarising power						
			Al-Cl bond has significant covalent character, hence AlCl ₃ has a simple molecular structure						
	High melting points because	e :	Low melting points because:						
	Large amount of energy is strong ionic bonds.	needed to overcome the	Small amount of energy is needed to overcome the vinstantaneous dipole-induced dipole interactions		<u>lar</u>				
Melting point	Melting points of NaC1 > Mg	C l₂ because:	Melting points of PC ℓ₅ > SiC ℓ₄ because:						
of chlorides	Mg ²⁺ has <u>higher</u> ionic charadius than Na ⁺	arge and <u>smaller</u> ionic	More electrons in PC l ₅ molecule than SiC l ₄ Increase in polarisability of electron cloud						
	Mg ²⁺ has a higher charge polarising power	density and hence <u>higher</u>	-						
	MgCl ₂ has some covalent ionic bonds in MgCl ₂ .	character, weakening the							

3.3 Reactions of Period 3 Oxides with Water, Acids and NaOH

LO (d) (iv) describe and explain the acid/base behaviour of oxides (for Na₂O; MgO; Al₂O₃; SiO₂; P₄O₁₀; SO₃) and hydroxides (for NaOH; Mg(OH)₂; Al(OH)₃), including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids

Graph 9: Trend of pH of Resulting Solution when Period 3 Oxides React with Water



				Na2O NIGO A12O3 SIC		
Period 3 oxide	Na₂O	MgO	A l ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO₃
Structure		Giant ionic structure		Giant molecular structure	Simple molec	cular structure
Reaction with water	reacts with H ₂ O by acception of respective to the control of the	D → 20H ⁻ (aq)	No reaction Al ₂ O ₃ does not dissolve in water because of its extremely high lattice energy. Large amount of energy is required to break the strong ionic bonds.	SiO ₂ does not dissolve in water because large amount of energy is required to break the strong and extensive covalent bonds between Si and O atoms.	with H ₂ O to give X—0 dissociate to give H ⁺ .	Dissolves in water to form H ₂ SO ₄ SO ₃ (g) + H ₂ O(l) → H ₂ SO ₄ (aq) C (X = S, P), which reacts between an and water Period H H H C H H C H H C H H C H H H C H H H C H H H C H
	pH 14	pH 9	pH 7	pH 7	pH 2	pH 2

Period 3 oxide	Na₂O	MgO	A 1₂O₃	SiO ₂	P ₄ O ₁₀	SO₃
Structure	Giant ionic structure			Giant molecular Simple molecular structure structure		cular structure
Nature of oxide	Basic		Amphoteric (i.e. shows both acidic and basic properties)	Acidic		
Decetion with	Forms salt and water	Forms salt and water	Forms salt and water	No reaction		
Reaction with acid	Na ₂ O(s) + 2HC l (aq) \rightarrow 2NaC l (aq) + H ₂ O(l)	MgO(s) + 2HC l (aq) \rightarrow MgC l 2(aq) + H ₂ O(l)	$Al_2O_3(s) + 6HCl(aq)$ $\rightarrow 2AlCl_3(aq) + 3H_2O(l)$			
Reaction with	<u>No re</u>	<u>action</u>	Dissolves in <u>excess</u> <u>NaOH</u> to form <u>colourless complex</u> , <u>Al(OH)₄-(aq)</u>	Reacts with hot conc. NaOH to form Na ₂ SiO ₃ (aq)	Forms salt and water	Forms salt and water
base			$Al_2O_3(s) + 2NaOH(aq)$ + $3H_2O(l)$ $\rightarrow 2NaAl(OH)_4 (aq)$	SiO ₂ (s) + 2NaOH(conc) \rightarrow Na ₂ SiO ₃ (aq) + H ₂ O(l)	$P_4O_{10}(s) + 12NaOH(aq)$ $\rightarrow 4Na_3PO_4(aq) +$ $6H_2O(l)$	$SO_3(g) + 2NaOH(aq)$ $\rightarrow Na_2SO_4(aq) + H_2O(l)$

Period 3 hydroxide	NaOH	Mg(OH) ₂	A/(OH) ₃
Structure		Giant ionic structure	
Nature of oxide	Ва	Amphoteric (i.e. shows both acidic and basic properties)	
Reaction with	Forms salt and water	Forms salt and water	Forms salt and water
acid	NaOH(aq) + H ⁺ (aq) \rightarrow Na ⁺ (aq) + H ₂ O(l)	$Mg(OH)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + 2H_2O(1)$	$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$
Reaction with base	No rea	Dissolves in <u>excess NaOH</u> to form <u>colourless</u> <u>complex</u> , $Al(OH)_4$ (aq) $Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4$ (aq)	

3.4 Reactions of Period 3 Chlorides with Water

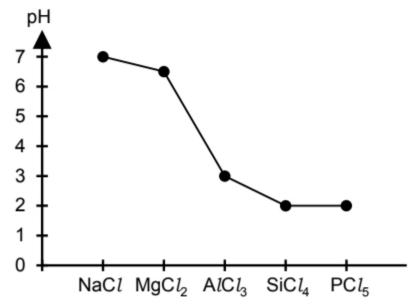
LO (d) (v) describe and explain the reactions of the chlorides with water (for NaC1; MgC12; A1C13; SiC14; PC15)

The reactions of Period 3 chlorides with water involve **hydration** and **hydrolysis** to different extents.

Across the third period as the chlorides become more covalent, tendency to undergo hydrolysis increases.

Period 3 chlorides	NaC1	MgC <i>l</i> ₂	Al	C <i>1</i> ₃	SiC14	PC <i>1</i> ₅
Structure		Ionic		Simple molecular		
Hydration The physical attraction between the cations and anions with the negative dipole and positive dipole of the water molecules, respectively (i.e. the formation of ion-dipole interactions).	* MC l_n (s) $\xrightarrow{H_2O(l)}$ No. No. No. No. No. No. No. No.	ons Na ⁺ (aq), Mg ²⁺ (aq) and es surround and form dativ $ \begin{bmatrix} QH_2 \\ H_2Q_{1,1}, & QH_2 \\ H_2Q_{2}, & QH_2 \\ H_2Q_{3}, & QH_2$	l^{-} (aq) l^{-} (aq) l^{-} (aq) l^{-} l^{-} $l^$		oes <u>not</u> undergo hydration	
The chemical	[Na(H ₂ O) ₆]⁺ does <u>not</u> undergo hydrolysis	[Mg(H ₂ O) ₆] ²⁺ undergoes slight hydrolysis	extensive hydrolysis		vacant and energetically	
reaction of the cation or covalent chlorides and water molecules such that the O-H bond in the water molecule is cleaved, giving H ₃ O ⁺ ions.		cation polarises the surrounding water and breaking the Orelease of a proton. [Al(H ₂ O) ₆] ³⁺ undergo	goes more extensive $(H_2O)_6]^{2+}$ as $A\ell^{3+}$ has a	to accept the lone pair from Think: Does CC14 under CC14 does not hydrolyst vacant orbitals for dative In addition, C atom is second to the control of the c	and energetically access om H ₂ O molecules, forming rgo hydrolysis? e in water as C has no en re bonding with H ₂ O molecules small and is shielded by sily attack the central C ato	g a dative bond. ergetically accession ules. larger C1 atoms. H

Graph 10: Trend of pH of Resulting Solution when Period 3 Chlorides React with Water



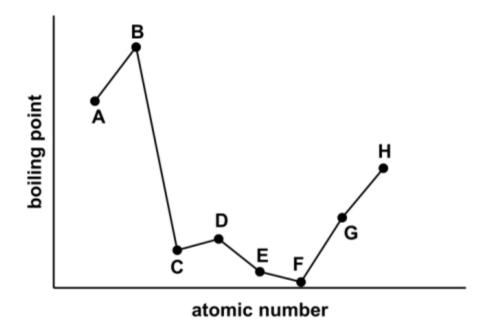
Period 3 chlor	ides	NaC1	MgC ℓ₂	All	C <i>l</i> ₃	SiC14	PC <i>1</i> ₅
Observations		Dissolves completely in water	Dissolves completely in water	<u>Dissolves</u> <u>completely</u> in <u>excess</u> water	Reacts vigorously with water, and forms white solid with white fumes of HC1 in limited amount of water	Reacts vigorously with water, and forms white solid with white fumes of HC1	Reacts vigorously with water, and forms white fumes of HC1
	hydration	NaCl(s) + aq → Na+(aq) + Cl-(aq) (hydration)	MgC $l_2(s)$ + 6H ₂ O(l) → [Mg(H ₂ O) ₆] ²⁺ (aq) + 2C l -(aq) (hydration)	In excess water: $AlCl_3(s) + 6H_2O(l)$ $\rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ (hydration)			
Reactions	hydrolysis	(no hydrolysis)	$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons$ $[Mg(H_2O)_5(OH)]^{+}(aq) +$ $H^{+}(aq)$ $(slight\ hydrolysis)$ $\begin{bmatrix} H^{H} & H^{-} & $	$[Al(H2O)6]3+(aq) \rightleftharpoons$ $[Al(H2O)5(OH)]2+(aq) +$ $H+(aq)$ (extensive hydrolysis) $\begin{bmatrix} H^{H} & H^{-} & H^{-} & H^{-} \\ H^{-} & H^{-} & H^{-} & H^{-} \\ \end{bmatrix}$	In limited supply of water: $AlCl_3(s) + 3H_2O(l) \rightarrow$ $Al(OH)_3(s) + 3HCl(g)$ (complete hydrolysis) or $2AlCl_3(s) + 3H_2O(l) \rightarrow$ $Al_2O_3(s) + 6HCl(g)$ (complete hydrolysis)	SiCl ₄ (l) + 2H ₂ O(l) → SiO ₂ (s) + 4HCl(aq) (complete hydrolysis)	PC <i>l</i> ₅ (s) + 4H ₂ O(<i>l</i>) → H ₃ PO ₄ (aq) + 5HC <i>l</i> (aq) (complete hydrolysis)
pH of solution	on	pH 7	pH 6.5	рН	13	pH 2	pH 2

Checkpoints for Section 3

- * To explain in terms of structure and bonding the physical properties of Period 3 elements and its oxides and chlorides.
- * To state and explain the variation in the highest oxidation number of the elements in oxides (for Na₂O; MgO; A₂O₃; SiO₂; P₄O₁₀; SO₃) and chlorides (for NaC1; MgC1₂; A₁C1₃; SiC1₄; PC1₅)
- * To state and explain the variation in bonding in oxides and chlorides in terms of electronegativity (with the exception of AlCl₃)
- * To describe the reactions of the oxides with water (for Na₂O; MgO; Al₂O₃; SiO₂; P₄O₁₀; SO₃), including writing of equations
- * To describe and explain the acid/base behaviour of oxides (for Na₂O; MgO; A₂O₃; SiO₂; P₄O₁₀; SO₃) and hydroxides (for NaOH; Mg(OH)₂; A₁(OH)₃), including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids, including writing of equations
- * To describe and explain the reactions of the chlorides with water (for NaCl; MgCl2; AlCl3; SiCl4; PCl5), including writing of equations
- * To suggest the types of structure and bonding present in the oxides and chlorides from observations of their chemical and physical properties

Example 3A

1 The graph below shows the variation in the boiling points for eight consecutive elements in the Periodic Table, all with atomic number between 10 and 20. Which of the following statements is true?



- A Element D forms an acidic oxide.
- B Element G does not conduct electricity.
- C Element A and beryllium are in the same group.
- D The element immediately preceding A has a smaller atomic radius than A.

HCI2011/1/13

Example 3A (continued)

2 Describe the reactions, if any, of the chlorides NaCl, AlCl₃ and PCl₅ with water.

Write equations for all reactions that occur, and suggest the pH of the resulting solutions.

Relate the reactivity of these chlorides to their structure and bonding.

NaCl has a ______, held together by ______. As a result, NaCl ______, where the ions undergoes hydration:

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

Due to the very low charge density of the hydrated Na⁺(aq) ion, no hydrolysis takes place and the pH of the resulting solution is ____.

AlCl₃ has a ______, containing intramolecular polar Al-Cl covalent bonds. As a result, AlCl₃ _____ with wate

In limited supply of water:

 $AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$ or

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

It undergoes ______to give white solid with white fumes of HCl.

Some of the HCl dissolves in water to give a pH of ____ for the resulting solution.

In excess water:

AICI₃

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

(hydration)

 $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

(extensive hydrolysis)

Due to the extensive hydrolysis of $[Al(H_2O)_6]^{3+}$ (aq), the pH of the resulting solution is . ____

PC l₅ has a ______, consisting of PC l₅ molecules containing intramolecular polar P–C l covalent bonds. As a result, PC l₅ ______with water.

 $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

It undergoes ______to give white fumes of HC1.

Due to some of the HCl dissolving in the water with the H₃PO₄ formed, the resulting solution is highly acidic at pH ____.

N19/3/4a

4 Diagonal Relationship

LO (e) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity

A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the **second and third periods** of the Periodic Table. Each of these pairs (Li and Mg, Be and A*l*, and B and Si) are said to exhibit similar properties and hence they have **diagonal relationships**.

Group 1	Group 2		Group 13		Group 14		
Li 🔪	Ве	/		В	/		С
Na	Mg		<u> </u>	Αl		^	Si

Diagonal relationships occur because

- (i) the elements have similar <u>electronegativity</u> (electronegativity increases across the period and decreases down the group)
- (ii) their cations have similar charge density (charge increases across the period and radius increases down the group)

Diagonal Relationship between Be and A1

Be and Al have similar electronegativity, and Be²⁺ and Al³⁺ have similar charge density.

When BeCl ₂ and AlCl ₃ dissolved in waterions undergo hydrolysis to give an aci	er, both Be ²⁺ (aq) and Al ³⁺ (aq) aqua complex dic solution.	Both BeO and Al ₂ O ₃ are amphoteric oxides that react with both acids and bases.		
BeC l_2 + 4H ₂ O \rightarrow [Be(H ₂ O) ₄] ²⁺ + 2C l^-	$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$	BeO + 2HC $l \rightarrow$ BeC l_2 + H ₂ O	$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$	
[Be(H ₂ O) ₄] ²⁺ \rightleftharpoons [Be(H ₂ O) ₃ (OH)] ⁺ + H ⁺	$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$	BeO + 2NaOH + H ₂ O \rightarrow Na ₂ Be(OH) ₄	$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$	

Diagonal Relationship between Li and Mg

Group 1 nitrates decompose to give nit	rite and oxygen: NaNO ₃ → NaNO ₂ + ½O ₂	Group 1 metal hydroxides and metal carbonate are thermally stable.		
However, LiNO ₃ is similar to Mg(NO ₃) ₂ metal oxide, NO ₂ and O ₂ .	which decomposes on heating to give	However, LiOH and Li ₂ CO ₃ decompose to form oxides similar to Mg(OH) ₂ and MgCO ₃ .		
$2LiNO_3 \rightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$ $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$		$2\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$	$Mg(OH)_2 \rightarrow MgO + H_2O$	
		$Li_2CO_3 \rightarrow Li_2O + CO_2$	$MgCO_3 \rightarrow MgO + CO_2$	

5 Group 2 Elements

5.1 Trend and Properties of Group 2 Elements

- LO (b) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity down a Group in terms of increasing number of electronic shells and nuclear charge
 - (f) describe and deduce from E^{\ominus} values the relative reactivity of elements of Group 2 as reducing agents

Element	Atomic No.	Electronic Configuration	Atomic and ionic radius	First I.E.	Electronegativity	Melting point
Ве	4	[He] 2s ²	Down the group, ** Both nuclear charge and shielding effect increase ** However, valence electrons are located in a shell with a larger principal quantum number, n, and are further away from the nucleus			Group 2 metals have giant metallic lattice structure with strong metallic bonds between the metal cations and sea of delocalised
Mg	12	[Ne] 3s ²	Weaker electrostatic forces of attraction between the nucleus and the valence electrons	Weaker electrostatic forces of attraction between the nucleus and the valence electrons	Weaker electrostatic forces of attraction between the nucleus and the electron pair in a	electrons. Down the group,
Ca	20	[Ar] 4s ²	Atomic and ionic radius increases	Less energy needed to remove the valence electron First I.E. decreases	covalent bond * Electronegativity decreases	 Size of cations increases Charge density decreases Weaker electrostatic
Sr	38	[Kr] 5s ²				force of attraction between the cations and sea of delocalised electrons
Ва	56	[Xe] 6s ²				 Less energy is required to overcome the weaker metallic bonds Melting point decreases

Group 2 element	Atomic No.	Electronic Configuration	Reducing power/ Chemical reactivity
Ве	4	[He] 2s ²	Down the group, ** Atomic radius increases ** Weaker electrostatic force of attraction between the nucleus and valence electrons ** Metal atoms lose their valence electrons to form M²+ cations more easily ** Creater tendency to be exidiced and reducing power/ observed reportivity increases down the group.
Mg	12	[Ne] 3s ²	** Greater tendency to be oxidised and reducing power/ chemical reactivity increases down the group Evidence: The standard electrode potential, E^{\oplus} value becomes more negative down the group. $\underline{E^{\oplus}}$ $Mg^{2+}(aq) + 2e^{-} \rightleftharpoons Mg(s) -2.37 \text{ V}$
Са	20	[Ar] 4s ²	$Ca^{2+}(aq) + 2e^{-} \rightleftharpoons Ca(s) -2.87 \text{ V}$ $Sr^{2+}(aq) + 2e^{-} \rightleftharpoons Sr(s) -2.89 \text{ V}$ $Ba^{2+}(aq) + 2e^{-} \rightleftharpoons Ba(s) -2.91 \text{ V}$
Sr	38	[Kr] 5s ²	More negative E^{\oplus} value \Rightarrow greater tendency to be oxidised \Rightarrow stronger reducing power $M^{2+}(aq) + 2e^{-} \rightleftharpoons M(s)$
Ва	56	[Xe] 6s ²	 Tendency for M²+(aq) to be reduced to M decreases Tendency for Group 2 metals to be oxidised to M²+ increases Reducing power of Group 2 metals increases Reactivity of Group 2 elements increases (e.g. Ba is more reactive than Mg) Note: Details about what the E[⊕] value represents will be covered in the topic of Electrochemistry in JC2.

5.2 Thermal Stability of Group 2 Oxysalts

LO (g) describe and explain the trend in thermal stability of Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion

An oxyanion, or oxoanion, is an oxygen-containing polyatomic anion with the generic formula $A_xO_y^{z^-}$, where A is another element. Oxyanions such as $CO_3^{z^-}$, NO_3^- , $SO_4^{z^-}$, IO_3^- and OH^- are generally **thermally unstable**, **decomposing on heating** to form **oxides**. The thermal stability of the Group 2 oxysalts is dependent on the following factors:

- (i) size and charge of cation
- (ii) size of oxyanion

Group 2 carbonates, nitrates and hydroxides decomposes in the following manner:

Carbonates:	MCO ₃ (s)	→	MO (s) + CO ₂ (g)
Nitrates:	$M(NO_3)_2$ (s)	\rightarrow	MO (s) + 2NO ₂ (g) + $\frac{1}{2}$ O ₂ (g)
Hydroxides:	M(OH) ₂ (s)	→	MO (s) + H₂O (g)

Concept of Thermal Decomposition of Group 2 Carbonates

The **thermal stability** of Group 2 carbonates **increases** down the group. In other words, the **thermal decomposition temperature** of Group 2 carbonates **increases** down the group.

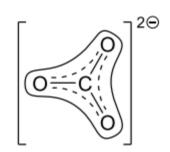
Down the group,

- * size of cations increases (while charge remains unchanged)
- * charge density (and polarising power) of the cations decreases
- electron cloud of CO₃²⁻ is <u>polarised (or distorted) to a lesser</u> extent
- C-O bond is weakened to a <u>lesser extent</u>.

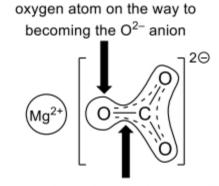
Hence, thermal stability of group 2 carbonates <u>increases down the</u> <u>group</u>.

As seen from the figure on the right, group 2 carbonates with cations of higher charge density (e.g. Mg²⁺) tend to undergo thermal decomposition more easily due to the greater polarisation (or distortion) of the large CO₃²⁻ electron cloud, which weakens the C–O bond to a greater extent.

Hence, MgCO₃ is less thermally stable than BaCO₃.

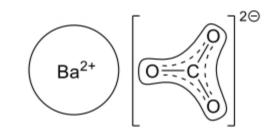


The electron cloud of CO_3^{2-} ion before polarisation.



delocalised electrons being pulled towards the positive charge, weakening C-O bond

As the electron cloud of CO_3^{2-} ion is large, it is greatly polarised by the Mg²⁺ ion (of higher charge density).



The electron cloud of CO₃²⁻ ion is less distorted by the Ba²⁺ ion, as it has a lower charge density than Mg²⁺.

Checkpoints for Section 5

- * To describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity down Group 2 in terms of increasing number of electronic shells and nuclear charge
- To describe and deduce from E

 values the relative reactivity of elements of Group 2 as reducing agents.

 ** To describe and deduce from E

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- * To describe and explain the trend in thermal stability of Group 2 carbonates in terms of the charge density of the cation and the ease of distortion (or polarisability) of the large anion, including writing of equations

Example 5A

1 Which factors help to explain the increase in thermal stability of the carbonates of Group 2 metals from magnesium to barium?

	charge density of cation	relative polarisability of carbonate and oxide ions
Α	decreases	CO ₃ ²⁻ less than O ²⁻
В	decreases	O^{2-} less than CO_3^{2-}
С	increases	CO_3^{2-} less than O^{2-}
D	increases	O ²⁻ less than CO ₃ ²⁻

N03/I/16

2 Use of the Data Booklet is relevant to this question.

Lead(II) carbonate and zinc carbonate decompose on heating in the same way as calcium carbonate.

What will be the predicted order of decomposition temperatures of these three carbonates?

	highest				lowest
Α	CaCO₃	>	PbCO ₃	>	ZnCO ₃
В	CaCO₃	>	ZnCO ₃	>	PbCO ₃
С	PbCO ₃	>	CaCO₃	>	ZnCO ₃
D	ZnCO ₃	>	CaCO₃	>	PbCO ₃

N02/I/15

6 Group 17 Elements

6.1 Trend and Properties of Group 17 Elements

Element	Structure and bonding	Dailing maint/ Valatility	Colour				
		Boiling point/ Volatility \(\begin{pmatrix} \text{volatility} \infty \frac{1}{\text{boiling point}} \end{pmatrix}	at r.t.p.	In gaseous state	In aqueous state	In organic solvent (e.g. hexane, CC14)	
C <i>l</i> ₂	Simple molecular structure	Down the group, ** Number of electrons increases	Greenish yellow gas	Greenish yellow	Pale yellow	Pale yellow	
Br ₂	Weak instantaneous dipole-induced dipole (id-id) interactions	Polarisability of electron cloud increases More energy required to overcome the stronger	Reddish brown liquid	Reddish brown	Orange	Orange-red	
I ₂	between the non-polar X ₂ molecules	intermolecular id-id interactions * Higher boiling point/lower volatility	Black solid	Purple	Brown	Purple	

LO (f) describe and deduce from E^{\oplus} values the relative reactivity of elements of Group 17 as oxidising agents

Element	Oxidising power and reactivity	Displacement reaction		
	Down the group, Size of atoms increases/ Atomic radius increases Decrease in tendency for X ₂ to accept electrons. Decrease in tendency for X ₂ to be reduced to X ⁻ . Oxidising power of halogens decreases	 Oxidising power of Cl₂ > Br₂ > I₂ The more reactive halogens, X₂ (higher up in the group) can displace the less reactive halides, X⁻ (lower down the group) from their aqueous solutions 		
C <i>l</i> ₂	Evidence: The standard electrode potential, E^{\oplus} value becomes less positive down the group. $\underline{E^{\oplus}}$	Cl_2 can displace Br^- and I^- : $Cl_2 + 2Br^- \rightarrow Br_2 + 2Ct^-$ $Cl_2 + 2I^- \rightarrow I_2 + 2Ct^-$		
Br ₂	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) + 1.36 V$ $Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) + 1.07 V$ $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) + 0.54 V$	Br ₂ can displace I ⁻ : Br ₂ + 2I ⁻ \rightarrow I ₂ + 2Br ⁻		
I ₂	Less positive E^{\oplus} value \Rightarrow smaller tendency to be reduced \Rightarrow weaker oxidising power Note: Details about what the E^{\oplus} value represents will be covered in the topic of Electrochemistry in JC2.	I ₂ is the weakest oxidising agent of all the halogens. It cannot displace Ct and Br.		

Example 6A

When C12 and Br2 reacts with Na2S2O3, Na2SO4 is formed. However, when I2 reacts with Na2S2O3, Na2S4O6 is formed instead. Explain why this is so.

 Cl_2 and Br_2 are <u>stronger</u> oxidising agents and hence can oxidise S in $S_2O_3^{2-}$ to a <u>greater</u> extent – oxidation number of S increases from <u>+2</u> in $S_2O_3^{2-}$ to <u>+6</u> in SO_4^{2-} . In $S_2O_3^{2-}$ to a <u>smaller</u> extent – Oxidation number of S increases from <u>+2</u> in $S_2O_3^{2-}$ to <u>+2.5</u> in $S_4O_6^{2-}$.

6.2 Trend and Properties of Hydrogen Halides (HX)

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

Hydrogen halide	Structure and bonding	Boiling point	Thermal stability				
	Simple molecular structure Weak instantaneous	Down the group, ** Number of	When heated, $2HX(g) \rightarrow H_2(g) + X_2(g)$ Bond Bond Energy / kJ mol ⁻¹			Does not decompose	
HC1	dipole-induced dipole (id-id) and permanent dipole-permanent	electrons increases Polarisability of		H-Cl	431		on heating.
		electron cloud increases		H–Br	366		
	dipole (pd-pd) interactions between the	* More energy		H–I	299		
HBr	polar HX molecules	required to overcome the stronger id-id interactions * Higher boiling point	Down the group, ** Size of halogen atom increases ** Effectiveness of orbital overlap between H and X atoms decreases			Decomposes above 1000 °C.	
HI			 Bond strength of H–X decreases Bond energy of H–X decreases (i.e. H–X bond becomes weaker) Less energy required to break the H–X bond Thermal stability decreases 		Decomposes readily on heating, e.g. plunging a red hot wire into the gas.		

Checkpoints for Section 6

- * To describe and deduce from E^{\oplus} values the relative reactivity of elements of Group 17 as oxidising agents
- * To describe and explain the trend in thermal stability of Group 17 hydrides in terms of bond energies

Example 6B

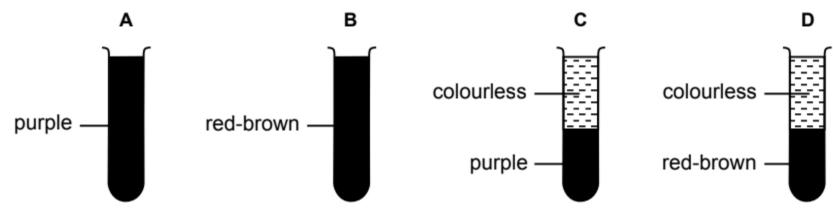
1 Group 17 elements and their hydrogen compounds exhibit trends in properties.

Which of these properties increases down the group $Cl \rightarrow Br \rightarrow I$?

- A the hydrogen-halogen bond dissociation energy
- **B** the oxidising power of the elements
- **C** the strength of the dispersion forces between halogen molecules
- D the thermal stability of hydrogen halides

N05/I/16

2 Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of trichloroethane.
Which observation would be made?



N96/IV/15

Appendix 1 New Elements Added to the Periodic Table

From: Science Daily (https://www.sciencedaily.com/releases/2016/01/160130182456.htm)

Robert Grzywacz, along with collaborators at Oak Ridge National Laboratory, developed the software used in the equipment that detects the new elements and helps analyze data from the experiments. He is a co-author of recent papers, representing a collaboration between US and Russian scientists, that present new data on elements 113, 115, 117, and 118.

The International Union for Pure and Applied Chemistry recently announced formal verification of the four new chemical elements and recognized ORNL for the discovery of two: 115, temporarily named ununpentium (Uup, element 115), and 117, temporarily named ununseptium (Uus, element 117).

The four new elements complete the seventh row of the periodic table.

"The super-heavy element research is one of the most interesting efforts in nuclear physics," said Grzywacz, a professor in the UT Department of Physics and Astronomy. "It concerns the core question of how protons and neutrons form bound systems -- the nuclei. For us experimentalists, it is a formidable experimental challenge because the synthesis of super-heavy elements is incredibly difficult. It takes a concerted effort of many people to make it work. It is a fantastic but very also very time- and labor- intensive research program."

Grzywacz is director of the UT-ORNL Joint Institute for Nuclear Physics and Applications (JINPA). He was formerly an ORNL Wigner Fellow.

rzywacz and the ORNL team developed a data acquisition technology that uses a new type of digital signal processing to measure very fast nuclear decays down to a microsecond -- one millionth of a second. Because the system was relatively untested, he and former UT postdoctoral researchers David Miller and Nathan Brewer tested and debugged the system, which resulted in a reliable process. The data acquisition system initially applied in the ORNL-based experiments was already used in studies searching for and detecting super-heavy nuclei in laboratories in Dubna, Russia, and Darmstadt, Germany.

The ORNL team worked with scientists from Russia and the United States on the discovery of two of the new elements. Russian scientists used actinide targets and intense 48Ca beams to manufacture new super-heavy elements. The ORNL group supplied the target material to produce the new elements, which can be synthesized only at an ORNL reactor facility. The UT-ORNL collaboration recently provided a new, more sensitive detection system used in experiments in Russia.

The ORNL team will have the honor of helping name elements 115 and 117. New elements can be named after a mythological concept, a mineral, a place or country, a property, or a scientist.

At the moment, there is no direct application for the two new elements because the quantities that can be produced are very small and unstable against decay, Grzywacz said. The properties of these elements may help scientists predict more new elements that can be synthesized, with some of them predicted to be more stable.

Grzywacz noted that one of the beauties of research is that every theoretical claim has to be verified experimentally.

"Experiments produce surprises for theories; theories make unexpected predictions for experiments," he said. "This will never stop. There will be always an exciting problem to solve -- and by the way, sometimes, and often unexpectedly, the solution is actually useful for everyone."

Further readings:



Names and symbols of four newly discovered elements announced



Is It Time to Upend the Periodic Table?