3.2 Periodic trends

Understandings:

- Vertical and horizontal trends in the Periodic Table exist for atomic radius, ionic radius, ionization energy, electron affinity, and electronegativity.

  Guidance
  Only examples of general trends across periods and down groups are required. For ionization energy the discontinuities in the increase across a period should be covered.
- Trends in metallic and non-metallic behaviour are due to the trends above.
- Oxides change from basic through amphoteric to acidic across a period.

Applications and skills:

- Prediction and explanation of the metallic and non-metallic behaviour of an element based on its position in the Periodic Table.
- Discussion of the similarities and differences in the properties of elements in the same group, with reference to alkali metals (Group 1) and halogens (Group 17).

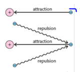
  Guidance
  Group trends should include the treatment of the reactions of alkali metals with water, alkali metals with halogens and halogens with halide ions.
- Construction of equations to explain the pH changes for reactions of Na_2O, MgO, P_4O_{10}, and the oxides of nitrogen and sulfur with water.

Physical properties

The elements in the Periodic Table are arranged to show how the properties of the elements repeat periodically. This **periodicity** of the elements is reflected in their physical properties. The atomic and ionic radii, electronegativity, and ionization energy are of particular interest as they explain the periodicity of the chemical properties.

The concept of effective nuclear charge is helpful in explaining trends in both physical and chemical properties.

Shielding and "effective nuclear charge"



Consider the main energy levels of a sodium atom:

sodium atom, Na 2,8,1

Across a period...

Element	Na	Mg	Al	Si
Nuclear charge	11	12	13	14
Electron configuration	[Ne] $3s^1$	[Ne] $3s^2$	[Ne] $3s^2 3p^1$	[Ne] $3s^2 3p^2$
Effective nuclear charge	≈ 11 – 10 ≈ +1	≈12 – 10 ≈+2	≈13 – 10 ≈+3	≈14 – 10 ≈+4

What relationship does this have with atomic radius?

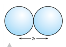


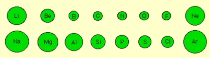
Figure 3.3 The atomic radius r is measured as half the distance between neighbouring nuclei.

Atomic radius is difficult to measure for a single atom as orbitals do not provide us with a set boundary for the outside of an atom.

We measure it by halving the distance between the nuclei of 2 bonded atoms.

As noble gases do not form bonds we ignore their atomic radii.

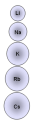
Trends in atomic radius in Periods 2 and 3



Down a group...

Element	Nuclear charge	Electron configuration
Li	3	$1s^2 2s^1$
Na	11	$1s^2 2s^2 2p^6 3s^1$
K	19	$1s^2 2s^2 2p^6 3s^1 3p^6 4s^1$

As we descend the group, the increase in the nuclear charge is largely offset by the increase in the number of inner electrons; both increase by eight between successive elements in the group. The effective nuclear charge experienced by the outer electrons remains approximately +1 down the group.



Ionic radius

The atomic and ionic radii of the Period 3 elements are shown in the table below.

Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius/10^{-12} m	186	160	143	117	110	104	99
Ionic radius/10^{-12} m	98 (Na^+)	65 (Mg^{2+})	45 (Al^{3+})	42 (Si^{4+}); 271 (Si^{4-})	212 (P^{3-})	190 (S^{2-})	181 (Cl^-)

Positive ion -->

Negative ions -->

Across the period, positive ions (Group 1-14) -->

Across the period, negatve ions (Group 14-17) -->

Down a group -->

Worked example

Describe and explain the trend in radii of the following atoms and ions:

O^{2-}, F^-, Ne, Na^+, and Mg^{2+}.

Solution

The ions and the Ne atom have 10 electrons and the electron configuration $1s^2 2s^2 2p^6$.

The nuclear charges increase with atomic number:

O: Z = +8
F: Z = +9
Ne: Z = +10
Na: Z = +11
Mg: Z = +12

The increase in nuclear charge results in increased attraction between the nucleus and the outer electrons. The ionic radii decrease as the atomic number increases.

Exercises

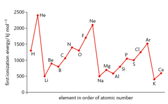
7 **(a)** Explain what is meant by the atomic radius of an element.
(b) The atomic radii of the elements are found in Table 9 of the IB data booklet.
(i) Explain why no values for ionic radii are given for the noble gases.
(ii) Describe and explain the trend in atomic radii across the Period 3 elements.

8 Si^{4+} has an ionic radius of 4.2×10^{-11} m and Si^{4-} has an ionic radius of 2.71×10^{-10} m. Explain the large difference in size between the Si^{4+} and Si^{4-} ions.

Ionisation energy

Definition - The energy required to remove 1 mole of electrons from 1 mole of a gaseous atoms in their ground state.

2 general trends -



Electron affinity

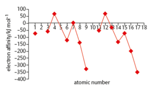
The first **electron affinity** of an element ($\Delta H^{\ominus}_{ea}$) is the energy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous ions:

$$X(g) + e^- \rightarrow X^-(g)$$

The 1st EA often releases a lot of energy (exothermic) whereas the 2nd onwards (3rd, 4th...) often require large amounts of energy (endothermic). Why?

Electron affinities can be thought of as the negative of first ionization energy of the anion.

- The Group 17 elements have incomplete outer energy levels and a high effective nuclear charge of approximately +7 and so attract electrons the most.
- The Group 1 metals have the lowest effective nuclear charge of approximately +1 and so attract the extra electron the least.



General trend -

Exceptions:

Group 2 -

Electronegativity

The **electronegativity** of an element is a measure of the ability of its atoms to attract electrons in a covalent bond (see Chapter 4). It is related to ionization energy as it is also a measure of the attraction between the nucleus and its outer electrons – in this case *bonding electrons*.

- Electronegativity increases from left to right across a period owing to the increase in nuclear charge, resulting in an increased attraction between the nucleus and the bond electrons.
- Electronegativity decreases down a group. The bonding electrons are furthest from the nucleus and so there is reduced attraction.

Group (vertical) / Period (horizontal)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.291		

Periodic table of electronegativity using the Pauling scale

10 Which of the following changes is endothermic?

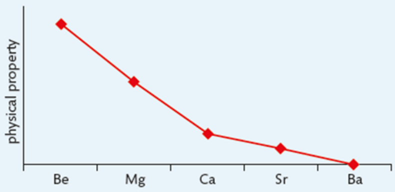
I $Ca(g) \rightarrow Ca^+(g) + e^-$
II $I(g) + e^- \rightarrow I^-(g)$
III $O^- + e^- \rightarrow O^{2-}(g)$

A I and II **B** I and III **C** II and III **D** I, II, and III

11 Identify the element which is likely to have an electronegativity value most similar to that of lithium?

A beryllium **B** sodium **C** magnesium **D** hydrogen

12 The graph represents the variation of a property of the Group 2 elements.



Identify the property.

A ionic radius **B** atomic radius **C** neutron/proton ratio
D first ionization energy

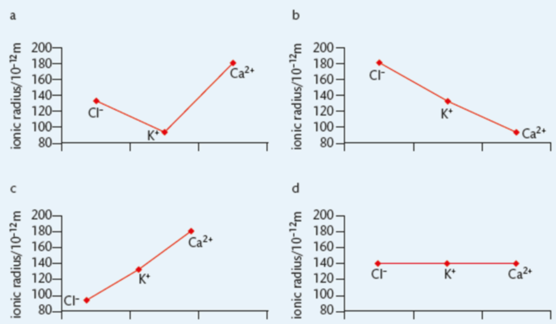
13 Atomic radii and ionic radii are found in the IB data booklet.

Explain why:

(a) the potassium ion is much smaller than the potassium atom.
(b) there is a large increase in ionic radius from silicon (Si^{4+}) to phosphorus (P^{3-}).
(c) the ionic radius of Na^+ is less than that of F^-.

Exercises

21 Identify the graph which shows the correct ionic radii for the isoelectronic ions Cl^-, K^+, and Ca^{2+}?



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Melting points

(more detail left until we have covered topic 4)

Element	Melting point / K	Element	Melting point / K
Li	454	F_2	54
Na	371	Cl_2	172
K	337	Br_2	266
Rb	312	I_2	387
Cs	302	At_2	575

Group 1 (alkali metals) Group 17 (halogens)

Chemical properties

The chemical properties of an element are determined by the electron configuration of its atoms. Elements of the same group have similar chemical properties as they have the same number of valence electrons in their outer energy level. The alkali metals in Group 1, for example, all have one electron in their outer shell and the halogens in Group 17 have seven outer electrons. The trends in their chemical properties can be accounted for by the trends in their properties discussed earlier.

Group 18

- Colourless gases
- Very unreactive
- Exist as single atoms

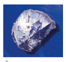
Group 1: the alkali metals

All the elements are silvery metals and are too reactive to be found in nature. They are usually stored in oil to prevent contact with air and water. The properties of the first three elements are summarized in the table below.

Physical properties	Chemical properties
• They are good conductors of electricity and heat. • They have low densities. • They have grey shiny surfaces when freshly cut with a knife.	• They are very reactive metals. • They form ionic compounds with non-metals.

Lithium is a soft reactive metal. When freshly cut, it has a metallic lustre. However, it rapidly reacts with oxygen in the air, giving it a dark oxide coat.

Sodium is softer and more reactive than lithium.



Potassium is softer and more reactive than sodium.

Write equations between Li, Na, K and water:

Why does universal indicator in the water turn blue?

(Hint: The acid-base character of a solution depends on the presence of H^+(acid) or OH^-(basic) ions.)

Reaction with water

The alkali metals react with water to produce hydrogen and the metal hydroxide. When you drop a piece of one of the first three elements into a small beaker containing distilled water, the following happens.

- Lithium floats and reacts slowly. It releases hydrogen but keeps its shape.
- Sodium reacts with a vigorous release of hydrogen. The heat produced is sufficient to melt the unreacted metal, which forms a small ball that moves around on the water surface.
- Potassium reacts even more vigorously to produce sufficient heat to ignite the hydrogen produced. It produces a lilac coloured flame and moves excitedly on the water surface.

Why?

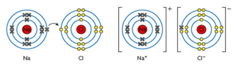
Group 17: the halogens

The Group 17 elements exist as diatomic molecules, X_2. Their physical and chemical properties are summarized in the table below.

Physical properties	Chemical properties
• They are coloured. • They show a gradual change from gases (F_2 and Cl_2), to liquid (Br_2), and solids (I_2 and At_2).	• They are very reactive non-metals. Reactivity decreases down the group. • They form ionic compounds with metals and covalent compounds with other non-metals.

Reactions with Group 1 metals:

Write a balanced equation between Na and Cl_2.



Which would be the most vigorous reaction between a halogen and group 1 metal?

Displacement reactions

The relative reactivity of the elements can also be seen by placing them in direct competition for an extra electron. When chlorine is bubbled through a solution of potassium bromide the solution changes from colourless to orange owing to the production of bromine:

$$2KBr(aq) + Cl_2(aq) \rightarrow 2KCl(aq) + Br_2(aq)$$

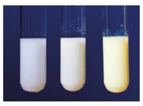
Reactions with silver nitrate can be used to identify the halide present:

The halides

The halogens form insoluble salts with silver. Adding a solution containing the halide to a solution containing silver ions produces a **precipitate** that is useful in identifying the halide ion.

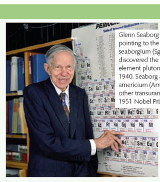
$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$$

This is shown in this photo.



NATURE OF SCIENCE

Element 117 would be a new halogen. Whereas the discovery of the early elements involved the practical steps of extraction and isolation often performed by one individual, later elements are made by teams of scientists working together. New elements are as much invented as discovered, but their existence provides further knowledge about the natural world. The first synthetic elements were the transuranics. They are radioactive elements which are heavier than uranium, the heaviest natural element.



Glenn Seaborg (1912–1999) pointing to the element seaborgium (Sg). Seaborg discovered the transuranic element plutonium (Pu) in 1940. Seaborg also discovered americium (Am) and seven other transuranics. He won the 1951 Nobel Prize in Chemistry.

Claims that a new halogen, element 117, had been made were first made in April 2010 but these findings have yet to be confirmed. Scientists publish their own results in scientific journals after their work has been reviewed by several experts working in the same field. This process is called peer review. If the element turns out to have the properties predicted of a halogen below astatine, it will provide more evidence to support our model of the atom and the Periodic Table.

Exercises

24 How do the reactivities of the alkali metals and the halogens vary down the group?

25 Which property of the halogens increases from fluorine to iodine?

A ionic charge **C** melting point of the element
B electronegativity **D** chemical reactivity with metals

26 Which pair of elements reacts most readily?

A Li + Br_2 **B** Li + Cl_2 **C** K + Br_2 **D** K + Cl_2

27 Chlorine is a greenish-yellow gas, bromine is a dark red liquid, and iodine is a dark grey solid. Identify the property which most directly causes these differences in volatility.

A the halogen–halogen bond energy
B the number of neutrons in the nucleus of the halogen atom
C the number of outer electrons in the halogen atom
D the number of electrons in the halogen molecule

28 A paper published in April 2010 by Yu. Ts. Oganessian and others claims the synthesis of isotopes of a new element with atomic number 117. One of the isotopes is $^{293}_{117}Uus$. Which of the following statements is correct?

A the nucleus of the atom has a relative charge of +117
B $^{293}_{117}Uus$ has a mass number of 117
C there are 262 neutrons in $^{293}_{117}Uus$
D the atomic number is 293 – 117

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Recap - Types of bonding

Bonding is determined using electronegativity values...

Ionic:

Covalent:

Simple covalent

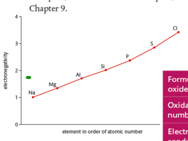
Giant covalent

Metallic:

Bonding of the Period 3 oxides

The conductivity of the molten oxides gives an experimental measure of their ionic character, as is shown in the table below. They only conduct electricity in the liquid state, when the ions are free to move.

Note that the maximum oxidation number of a Period 3 element is related to the group number. It is +1 for elements in Group 1, +2 for elements in Group 2, +3 for elements in Group 13, +4 for elements in Group 14, and so on. Oxidation numbers are discussed in Chapter 9.



Formula of oxide	$Na_2O(s)$	$MgO(s)$	$Al_2O_3(s)$	$SiO_2(s)$	$P_4O_{10}(s)$/ $P_4O_6(s)$	$SO_3(l)$/ $SO_2(g)$	$Cl_2O_7(l)$/ $Cl_2O(g)$
Oxidation number	+1	+2	+3	+4	+5/+3	+6/+4	+7/+1
Electrical conductivity in molten state	high	high	high	very low	none	none	none
Structure	giant ionic			giant covalent	molecular covalent		

Acid–base character of the Period 3 oxides

Formula of oxide	$Na_2O(s)$	$MgO(s)$	$Al_2O_3(s)$	$SiO_2(s)$	$P_4O_{10}(s)$/ $P_4O_6(s)$	$SO_3(l)$/ $SO_2(g)$	$Cl_2O_7(l)$/ $Cl_2O(g)$
Acid–base character	basic		amphoteric	acidic			

Basic oxides

Sodium oxide and magnesium oxide dissolve in water to form alka solutions owing to the presence of hydroxide ions:

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

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$$

Acidic oxides

The non-metallic oxides react readily with water to produce acidic solutions. Phosphorus(V) oxide reacts with water to produce phosphoric(V) acid:

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

Phosphorus(III) oxide reacts with water to produce phosphoric(III) a

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

Sulfur trioxide reacts with water to produce sulfuric(VI) acid:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Sulfur dioxide reacts with water to produce sulfuric(IV) acid:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

Dichlorine heptoxide (Cl_2O_7) reacts with water to produce chloric(VII) acid ($HClO_4$):

$$Cl_2O_7(l) + H_2O(l) \rightarrow 2HClO_4(aq)$$

Dichlorine monoxide (Cl_2O) reacts with water to produce chloric(I) acid (HClO):

$$Cl_2O(l) + H_2O(l) \rightarrow 2HClO(aq)$$

Silicon dioxide does not react with water, but reacts with concentrated alkalis to form silicates:

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

Amphoteric oxides

Aluminium oxide does not affect the pH when it is added to water as it is essentially insoluble. It has amphoteric properties, however, as it shows both acid and base behaviour. For example, it behaves as a base as it reacts with sulfuric acid:

and behaves as an acid when it reacts with alkalis such as sodium hydroxide:

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

Exercises

29 An oxide of a Period 3 element is a solid at room temperature and forms a basic oxide. Identify the element.

A Mg **B** Al **C** P **D** S

30 Which pair of elements has the most similar chemical properties?

A N and S **B** N and P **C** P and Cl **D** N and Cl

31 Identify the oxide which forms an acidic solution when added to water.

A $Na_2O(s)$ **B** $MgO(s)$ **C** $SiO_2(s)$ **D** $SO_3(g)$

32 (a) Use the data below to identify the state of the four oxides listed under standard conditions.

Oxides	Melting point / K	Boiling point / K
MgO	3125	3873
SiO_2(quartz)	1883	2503
P_4O_{10}	297	448
SO_2	200	263

(b) Explain the difference in melting points by referring to the bonding and structure in each case.

(c) The oxides are added to separate samples of pure water. State whether the resulting liquid is acidic, neutral, or alkaline. Describe all chemical reactions by giving chemical equations.

(d) Use chemical equations to describe the reactions of aluminium oxide with:

(i) hydrochloric acid

(ii) sodium hydroxide

33 Describe the acid–base character of the oxides of the Period 3 elements Na to Ar. For sodium oxide and sulfur trioxide, write balanced equations to illustrate their acid–base character.

32

	(a) State under standard conditions	(b) Structure and bonding
MgO	(s)	giant structure ionic bonding; strong attraction between oppositely charged ions
SiO_2 (quartz)	(s)	giant structure covalent bonding; strong covalent bonds throughout structure
P_4O_{10}	(s)	molecular, covalent bonding; weak intermolecular forces between molecules; P_4O_{10} is larger molecule and so has stronger London dispersion forces and a higher melting point than SO_2
SO_2	(g)	molecular, covalent bonding; weak intermolecular forces between molecules; SO_2 is smaller molecule and so has weaker London dispersion forces and a higher melting point than P_4O_{10}

What is the effective nuclear charge for the outer electron in an atom of O, Mg and He?