PHYSICAL PERIODICITY OF ELEMENTS

Content:

Periodicity of atomic properties of the elements: variation with proton number across the third period (sodium to chlorine) and down the group of:

- atomic radius and ionic radius
- ionisation energy
- electronegativity

Learning Outcomes required for H1 (8873) Chemistry:

Trends and variations in atomic properties

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

(l) Recognize variation in the electronic configurations across a Period and down a Group.

(m) 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 filled electronic shells, shielding and nuclear charge

References

1. Hill, G. & Holman, J. (1992). *Chemistry in Context, 6th edition.* New York: Prentice Hall.
2. Ramsden, E. N. (1994). *A Level Chemistry, 3rd edition.* UK: Stanley Thornes (Publishers) Ltd.
3. Chemistry for Advanced Level, Peter Cann, Peter Hughes
4. A-level Chemistry, E.N. Ramsden

1 INTRODUCTION TO THE PERIODIC TABLE

Mankind had always been seeking to discover new chemical elements since centuries ago. As of January 2021, a total of 118 elements have been identified. Studying these hundreds of elements with different physical and chemical properties will surely be a daunting task, unless there is a systematic and organized way to do it. Much of what we will cover in this topic is credited to the Russian chemist Dmitri Ivanovich Mendeleev (1834-1907),whose seminal hypothesis that the *chemical and physical properties of the elements vary in a periodic way* laid the foundations of the modern Periodic Table.

The Periodic Table is a table of elements arranged by order of their atomic numbers in such a way that the periodic properties (chemical periodicity) of the elements are made clear. In fact, the Periodic Table is a masterpiece of organised chemical information.

The standard form of Periodic Table includes **periods** (horizontal rows) and **groups** (vertical columns). The elements in the same period have the same number of core electrons as that of the noble gas from previous period. **Elements in the same group have the same number of valence electrons and hence similar chemical properties.**

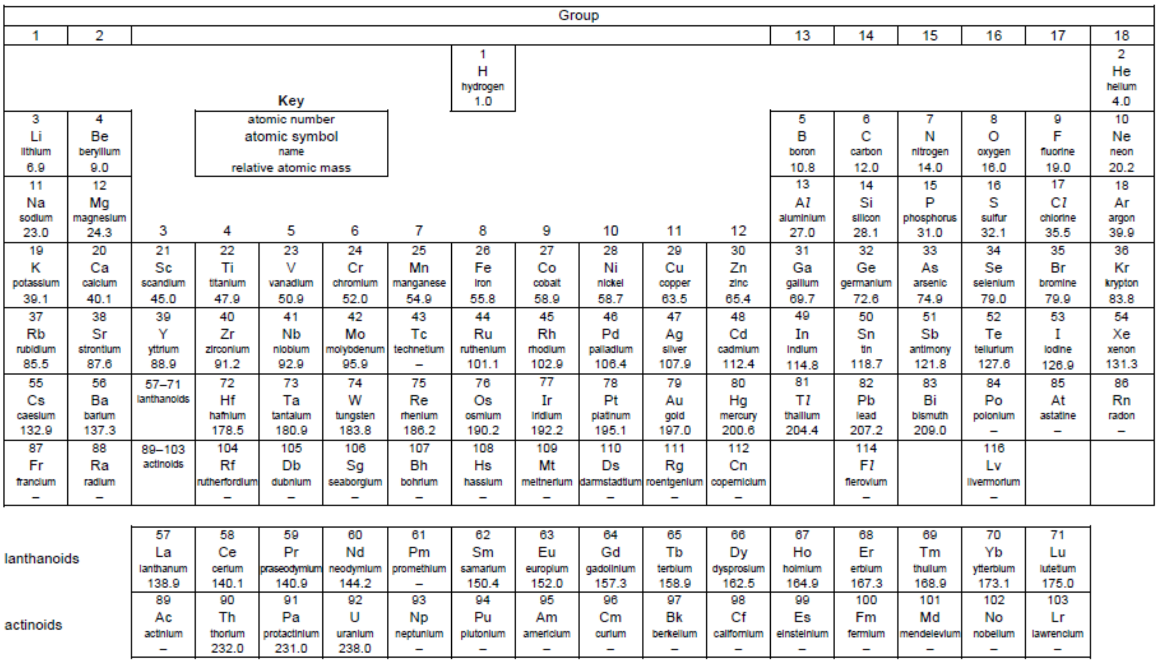
Physical periodicity is the study of periodic trends which indicate the tendencies of certain elemental characteristics to change as one progresses along a row or column of the Periodic Table.

The valence (outermost) shell electronic configuration of the elements can be used to determine the location of the element in the Periodic Table.

- The principal quantum number, “n”, of the valence shell indicates the **period** of the element.
- The number of valence electrons indicates the **group** of the element. (Note that elements with 3-8 valence electrons are in Group 13 to 18)

Group	Valence shell electronic configuration
1	ns^1
2	ns^2
13	$ns^2\ np^1$
14	$ns^2\ np^2$
15	$ns^2\ np^3$
16	$ns^2\ np^4$
17	$ns^2\ np^5$
18	$ns^2\ np^6$

For example, an element with the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \mathbf{4}s^2 \mathbf{4}p^5$ is located at **Period 4** of the Periodic Table and is in Group 17. The element is Br.



Group

Key
atomic number
atomic symbol
name
relative atomic mass

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 A*l* aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 C*l* chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 T*l* thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 F*l* flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

Checkpoint 1

Write the electronic configurations of (i) Li and Na and (ii) F and C*l*. Observe their relative positions on the Periodic Table. Underline the valence electronic configurations.

(i) Li : ______________ Na: ________________

(ii) F : ______________ C*l* : ______________________

2 FUNDAMENTAL CONSIDERATIONS IN IONISATION ENERGY AND PHYSICAL PERIODICITY

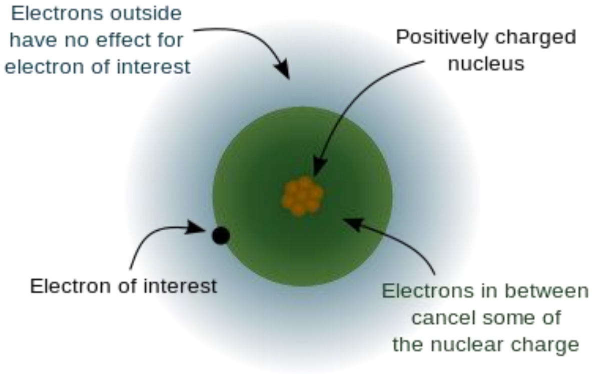
2.1 Nuclear charge

Nuclear charge is the total charge of all the protons in the nucleus. The larger the number of protons in the nucleus of an atom, the greater the nuclear charge. Hence, across a period or down a group, nuclear charge increases.

2.2 Shielding effect

Note:
Electrons in the same outer electronic shell exert negligible shielding effect.

Valence electrons in an atom do not only ‘feel’ attraction from the protons in the nucleus, but also repulsion from inner shells electrons. The ‘feel’ of repulsion from inner-shell electrons is called **shielding effect.** The inner-shell electrons shield the outer electron from the full charge of the nucleus. Shielding effect increases as the number of inner shell electrons increases.



2.3 Distance of electrons from nucleus

The larger the number of filled electronic shells an atom has, the further the valence electrons are from the nucleus, hence the weaker the attraction they experience from the proton in the nucleus.

2.4 Nuclear attraction

(“net attraction electrons experienced from the nucleus”)

Nuclear attraction refers to “attraction between the nucleus and the electrons (nuclear charge) – “repulsion between electrons (shielding effect) and distance of electrons from nucleus”

Nuclear attraction	**=**	**nuclear charge**	**–**	**shielding effect and distance of electrons from nucleus**

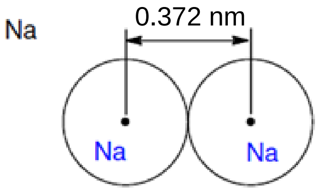
3 ATOMIC RADIUS (ATOMIC SIZE)

The **atomic radius** of an element is a measure of the size of its atoms, usually the mean distance from the nucleus to the boundary of space occupied by the valence electrons. Since the boundary is not a well-defined physical entity, there are various non-equivalent definitions of atomic radius. Some commonly used definitions of atomic radius include metallic radius, covalent radius and van der Waals radius.

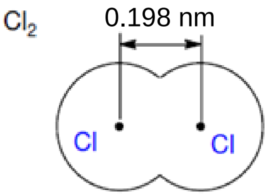
The ***metallic radius*** is defined as half the internuclei distance between the two adjacent metal atoms in the metallic lattice.

The ***covalent radius*** is defined as half the internuclei distance between two atoms which are covalently bonded. In principle, the sum of the two covalent radii should equal the covalent bond length between two atoms.

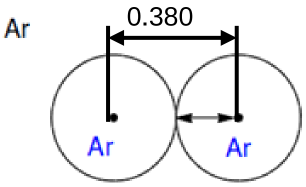
For noble gas such as He, Ne and Ar, the measured radius is known as the ***van der Waals radius*** as these noble gas atoms do not form covalent bond.



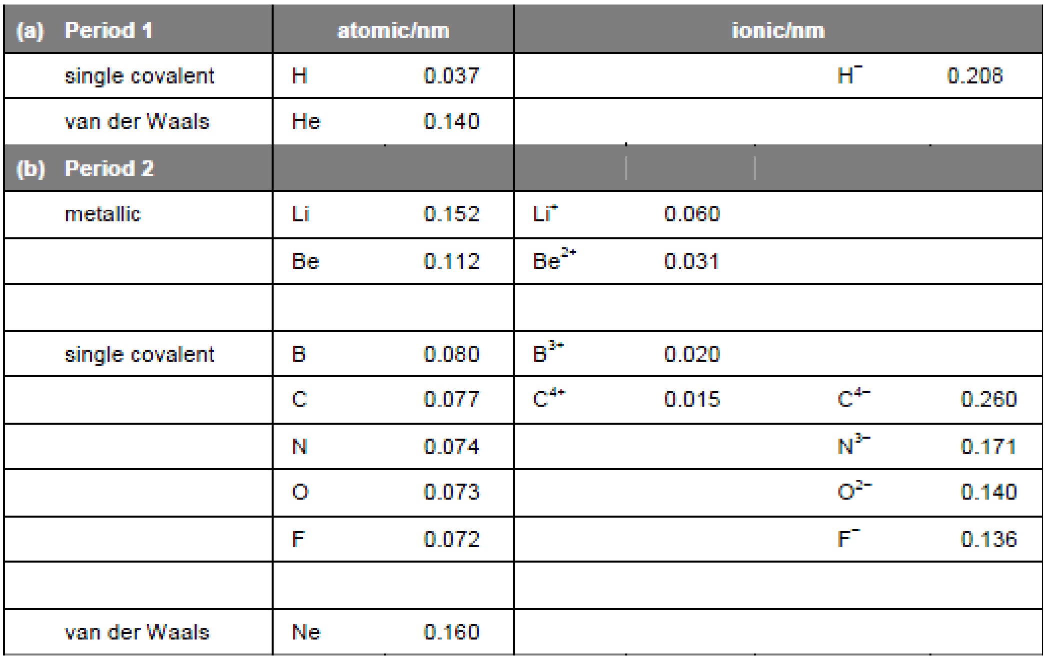
Metallic radius of Na
= 0.186 nm



Covalent radius of C*l*
= 0.099 nm



van der Waals radius of Ar
= 0.190 nm

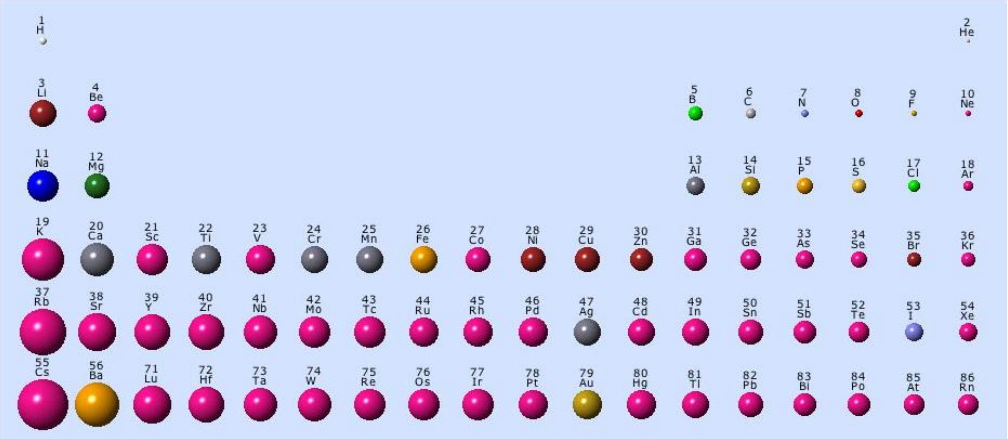


(a) Period 1	atomic/nm		ionic/nm			
single covalent	H	0.037			H^-	0.208
van der Waals	He	0.140				
(b) Period 2						
metallic	Li	0.152	Li^+	0.060		
	Be	0.112	Be^{2+}	0.031		
single covalent	B	0.080	B^{3+}	0.020		
	C	0.077	C^{4+}	0.015	C^{4-}	0.260
	N	0.074			N^{3-}	0.171
	O	0.073			O^{2-}	0.140
	F	0.072			F^-	0.136
van der Waals	Ne	0.160				

Atomic and ionic radii from the Data Booklet

In this section we refer atomic radius to the size of its atoms in general.

Atomic Size Trends



4 PERIODICITY TREND

4.1 Across the period

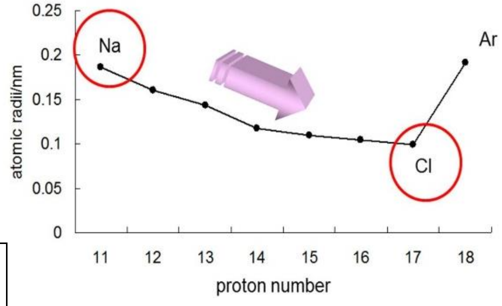
- **Atomic radius and Ionic radius**
- **Ionisation Energy**
- **Electronegativity**

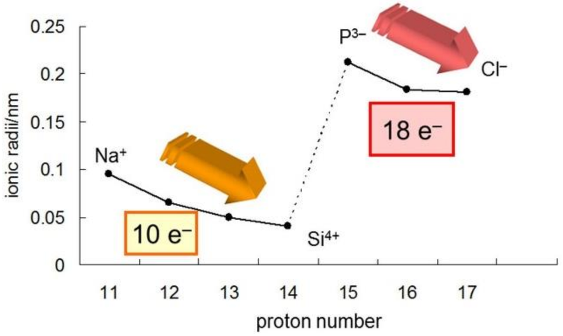
4.2 Down the group

- **Atomic radius and Ionic radius**
- **Ionisation Energy**
- **Electronegativity**

4.3 Sharp drop in first IE between Group 18 element and Group 1 element of the next period

Learning Outcome:
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 effect and nuclear charge
(ii) down a Group in terms of increasing number of electronic shells, shielding effect and nuclear charge

<table>
<tr><th>Period 3</th><th>Sodium
(Na)</th><th>Magnesium
(Mg)</th><th>Aluminium
(Al)</th><th>Silicon
(Si)</th><th>Phosphorus
(P)</th><th>Sulfur
(S)</th><th>Chlorine
(Cl)</th><th>Argon
(Ar)</th></tr>
<tr><td>Atomic radius</td><td colspan="8">Across the Period,
• Nuclear charge ______________ (due to increasing number of protons in the nucleus),
• Shielding effect remains ________________ (due to the same number of inner shell electrons)
• Nuclear attraction for the valence electrons __________(electrostatic forces of attraction between the nucleus and the valence electrons)
• The electrons are pulled closer to the nucleus, hence atomic radius __________ across the Period.


Note: For noble gas such as He, Ne and Ar, the measured radius is known as the <i>van der Waals radius</i> as these noble gas atoms do not form covalent bond. This is a different measurement from metallic radius and covalent radius and hence it does not follow the decreasing trend.</td></tr>
<tr><td>Ionic radius</td><td colspan="7">Na$^+$, Mg^{2+}, Al^{3+} and Si^{4+} are __________________ (same no. of electrons) with 10 electrons.
Similarly, P^{3-}, S^{2-} and Cl$^-$ are isoelectronic with 18 electrons each.
Across the isoelectronic species,
• Nuclear charge ____________
• Shielding effect remains _____________ (number of electrons remains the same).
• Nuclear attraction for the valence electrons ______________
• The electrons are pulled closer to the nucleus, hence ionic radius __________________ across each isoelectronic series.


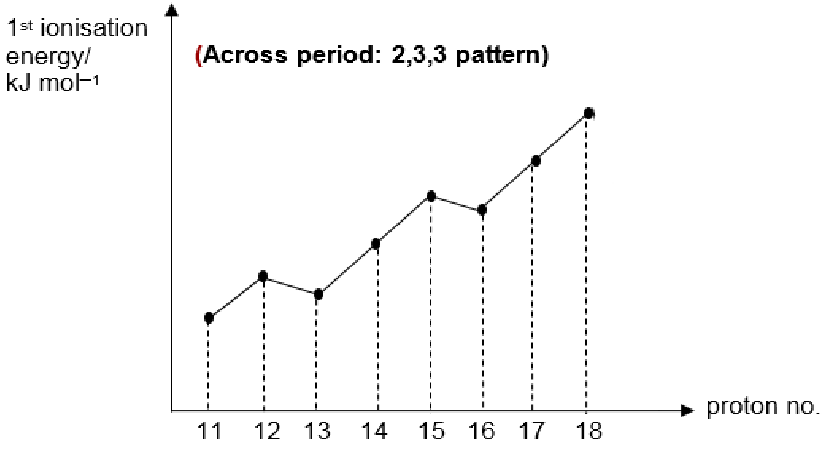
Note: There is a sharp increase in ionic radius from the cationic series of Na$^+$ to Si^{4+} to the anionic series of P^{3-} to Cl$^-$, as the anions have one more quantum shell of electrons than the cations.</td><td>Argon does not form ions</td></tr>
<tr><td>Electro negativity</td><td colspan="7">Electronegativity of an atom is a measure of its ability to attract the shared paired of electrons in a covalent bond towards itself.
Across the Period,
• Nuclear charge______________,
• Shielding effect remains ____________________,
• Nuclear attraction for the valence electron _____________, and thus on the shared pair of electrons in covalent bond.</td><td>Argon does not form covalent bonds</td></tr>
</table>

	• Electronegativity of the atom **increases across the Period.**							
Period 3	**Sodium (Na)**	**Magnesium (Mg)**	**Aluminium (A*l*)**	**Silicon (Si)**	**Phosphorus (P)**	**Sulfur (S)**	**Chlorine (C*l*)**	**Argon (Ar)**

First Ionisation energy (1^{st} I.E.)

In general, **first ionisation energy** of elements **increases across the Period**.

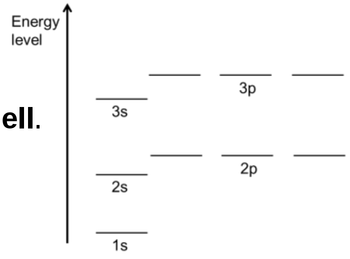
- **Nuclear charge** ______________ (due to increasing number of protons in the nucleus),
- **Shielding effect remains** ___________________ (due to the same number of inner shell electrons),
- **Nuclear attraction** for the valence electron ________________.
- **More energy** is required to remove the _________________electron and 1^{st} IE ______________**across the Period**.



Exceptions:

1. Small dip between Group 2 and Group 13 elements

Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ A*l*: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$



- The most loosely held electron of A*l* is in the **higher energy 3p subshell** while that of Mg is in the **3s subshell**.
- **Less energy** is required to remove the **most loosely held 3p** electron of A*l*, resulting in lower 1^{st} IE.

2. Small dip between Group 15 and Group 16 elements

P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	schematic diagram: ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿ ↿ ↿ 1s 2s 2p 3s 3p	• The most loosely held electron in S is in a **doubly filled 3p orbital** while that of P is in a singly filled 3p orbital. • This most loosely held electron in S experiences **inter-electron repulsion with its paired 3p electron**. • **Less energy** is required to remove this electron in S, resulting in lower 1^{st} IE.
S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	schematic diagram: ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿ ↿ 1s 2s 2p 3s 3p	

Checkpoint 2 

1 In which of the following pairs is the radius of the second atom greater than that of the first atom?

A Na, Mg **B** Sr, Ca **C** P, N **D** C*l*, Br

2 The following species contain the same number of electrons. In which order do their radii increase?

	smallest radius ----------------------> largest radius		
A	Ar	K^+	Ca^{2+}
B	Ca^{2+}	Ar	K^+
C	Ca^{2+}	K^+	Ar
D	K^+	Ar	Ca^{2+}

3 The following represents the electronic configuration of both a Group 2 cation and Group 17 anion.

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$$

The radius of the anion is about twice that of the cation.

Which reasons explain the difference in their sizes?

1 The cation has a greater nuclear charge than the anion.
2 Anion has a greater shielding effect than the cation.
3 On forming the anion from its atom, the extra electron repulsion makes the ion much bigger.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

Answer to Checkpoint 2 : DCD

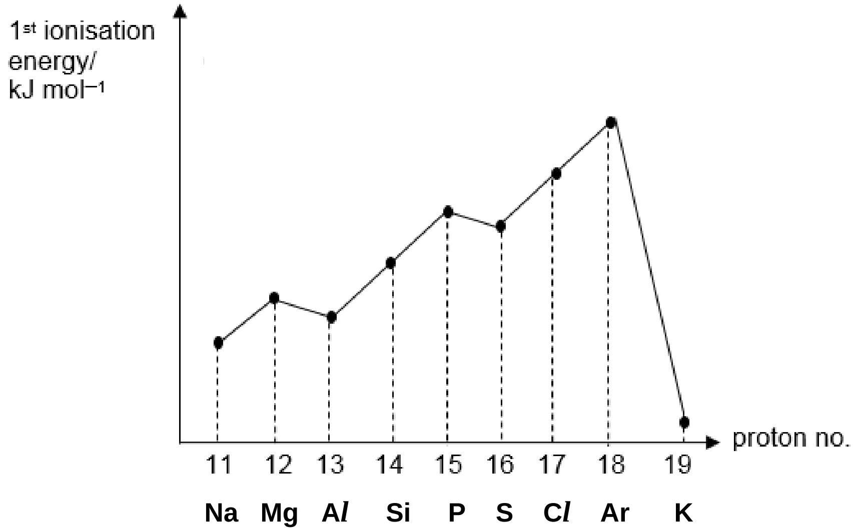
4.2 Periodicity Trend Down a Group

Element	**Atomic radius (nm)**	**Ionic radius (nm)**	**1st I.E. (kJ mol^{-1})**	**2nd I.E. (kJ mol^{-1})**	**3rd I.E. (kJ mol^{-1})**
Cl	0.099	0.181	1260	2300	3850
Br	0.114	0.195	1140	2080	3460
I	0.133	0.216	1010	1840	3200

Properties	**General Trend**	**Reasons**
Atomic radius and Ionic radius	Atomic radius and ionic radius **increases** down the group	Down the group, (1) The valence electron is **further away from the nucleus** due to having ______ **principal quantum shell.** (2) ______ **in shielding effect** (due to greater no. of inner core electrons) (3) These factors ______ **the increase in nuclear charge** (4) Decreasing nuclear attraction for: (i) the valence electrons. Hence electrons are less attracted to the nucleus and → **atomic/ionic radius** ______ (ii) the most loosely held electron → **ionisation energies** ______down the group. (iii) bonding pairs of electrons in a covalent bond → **electronegativity** ______.
Ionisation energy and Electronegativity	Ionisation energy and Electronegativity **decreases** down the group	

Note:
The concept of electronegativity is **useful in predicting if a bond formed is covalent or ionic** in the next topic of chemical bonding.

4.3 Sharp drop in first IE between Group 18 element and Group 1 element of the next period



Considering Ar ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) and K ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$).

- The **most loosely held 4s** electron in K is **further away from the nucleus** than that of Ar due to K having **1 more filled principal quantum shell**.
- K has a **greater shielding effect** (due to greater no. of inner core electrons)
- These factors **outweigh the higher nuclear charge in K.**
- The nuclear attraction for the most loosely held electron is weaker in K, thus **ionisation energy is lower for K.**

<u>Steps to answering questions relating to ionisation energy trend:</u>

1. Write down the electronic configuration of the respective species
2. Identify the position of the most loosely held electron of the respective species.
3. Identify which category does the comparison falls under

<u>General Trend</u>

(a) Same principal quantum shell **n**

(nuclear charge, shielding effect)

(b) Different principal quantum shell **n** vs **n+1**

(nuclear charge, shielding effect, no of filled principal quantum shell)

<u>Exception</u>

(c) Same principal quantum shell with configuration **ns^2 vs ns^2 np^1**

(s electron in a lower energy orbital)

(d) Same principal quantum shell with **ns^2 np^3 vs ns^2 np^4**

<u>Checkpoint 3</u>

1. Compare the difference in 1st ionisation energy between the following pairs of elements:

(i) Be and B

Electronic Configuration of Be: ______________ B: ______________

(category _____)

The most loosely held electron of B is in the ______________________**subshell** while that of Be is in the __________ **<u>subshell</u>**. **<u>Less energy</u>** is required to remove the ________________________**2p** electron, resulting in lower 1st IE.

(ii) S and C*l*

Electronic Configuration of S: ______________________ C*l*: ______________________

(category _____)

Most loosely held electron is removed from the ______________ subshell for both S and C*l*. **<u>Nuclear charge</u>** for S__________ than C*l*. **<u>Shielding effect</u>** for both S and C*l* are ____________ ______________, **<u>Nuclear attraction</u>** for the most loosely held electron in C*l* is _____________ than S. _________ energy is required to remove the most loosely held electron in C*l* and 1st IE higher.

Checkpoint 3 (Continued)

(iii) Ne and Na

Electronic Configuration of Ne: ________________ Na: ______________________
(category ______)

The ____________________ electron in Na is ____________ **from the nucleus** than that of Ne due to Na having ____________________ principal quantum shell**.** Na has a ________ **shielding effect.** These factors ___________ **the** ______ **nuclear charge in Na.** The nuclear attraction for the most loosely held electron is _______ in Na, thus **ionisation energy is ______for Na.**

(iv) N and O

Electronic Configuration of N: _________________ vs O: __________________
(category ______)

O has _________ nuclear charge but the most loosely held electron is in a _______________ **orbital** while that of N is in a **singly filled 2p** orbital. **Nuclear attraction** for the valence electron in O is _______ as the electron experiences _____________________________________ electron. _____ energy is required to remove **this most loosely held** electron in O, resulting in lower 1st IE.

2. Compare the difference in electronegativity between the following pairs of elements:

(i) C and N

N has ____________________ than C. N and C have _________________ **shielding effect**. _______________ for its valence electrons is ___________ thus the _________________ _________ in covalent bond in N is stronger. Thus, N has higher electronegativity.

(ii) F and C*l*

C*l* has ____________________ is higher than F. C*l* has ________________ **principal quantum shell** than F and hence the distance of valence electron is further away. **Nuclear attraction** the *valence electrons* in C*l* is ____________thus the ____________________C*l* in the covalent bond is weaker and C*l* has lower electronegativity.

	Success Criteria	√
	I am able to:	
(a)	Describe the trends and variations in atomic properties for elements in the • third period (sodium to chlorine), • Group 17 (chlorine to iodine)	
(b)	Recognize variations in the electronic configuration across a Period and down a Group.	
(c)	Describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity: (a) Across the Period - Same principal quantum shell **n** **(nuclear charge, shielding effect)**	
	(b) Down the Group - Different principal quantum shell **n** vs **n+1** **(nuclear charge, shielding effect, no of filled principal quantum shell)**	
(d)	Describe and explain qualitatively the exception cases in ionisation energy trend (i) Same principal quantum shell with configuration **ns^2 vs ns^2np^1** **(s electron in a lower energy orbital)**	
	(ii) Same principal quantum shell with **ns^2np^3 vs ns^2np^4** **(interelectronic repulsion between paired np electron)**	

Tutorial –Physical Periodicity of Elements

Periodic Trend -Atomic and Ioni Radii

1 Oxygen reacts with platinum(VI) fluoride, PtF_6, as follows.

$$O_2 + PtF_6 \longrightarrow O_2^+PtF_6^-$$

It was suggested that xenon should react similarly and in this way, the first noble gas compound was produced.

$$Xe + PtF_6 \longrightarrow Xe^+PtF_6^-$$

What is the most likely reason for the suggestion being made?

A O and Xe have similar atomic radii

B O and Xe have similar electron affinities.

C O_2 and Xe have similar electronic configurations.

D O_2 and Xe have similar first ionisation energies.

N2003/I/3

2 The elements radon (Rn), francium (Fr) and radium (Ra) have consecutive proton numbers in the Periodic Table.

What is the order of their first ionisation energies?

Least endothermic ⟶ Most endothermic

	Least endothermic		Most endothermic
A	Fr	Rn	Ra
B	Fr	Ra	Rn
C	Ra	Rn	Fr
D	Ra	Fr	Rn

N99/III/4; N2002/I/3

3 Gaseous particle **X** has a proton number n and a charge of +1.

Gaseous particle **Y** has a proton number of (n+1) and is isoelectronic (has the same number of electrons as) with **X**.

Which statements correctly describe **X** and **Y**?

1 **X** has a larger radius than **Y**.

2 **X** requires more energy than **Y** when a further electron is removed from each particle.

Periodic Trend – Ionisation Energy

4 Table 1 provides data on elements in Period 2 of the Periodic Table.

	Li	Be	B	C	N
No. of protons	3	4	5	6	7
Electronic configuration					
1st ionization energy/ kJ mol^{-1}	520	900	801	1086	1402

Table 2 shows the first 6 successive ionisation energies of an element **X**, which is in Period 3 of the Periodic Table.

	1st	2nd	3rd	4th	5th	6th
Ionisation energy / kJ mol^{-1}	578	1817	2745	11578	14831	18378

(a) **(i)** Fill in the electronic configuration of each element in Table 1.

(ii) Using Table 1, describe and explain the trend in first ionisation energies shown by the Period 2 elements, Li–N.

(b) Using Table 2, identify element **X**. Explain how you decided on your answer.

5 **(a)** Sketch a graph of the first I.E. of the elements sodium to potassium against proton number.

(b) Using the graph, explain the difference in the first I.E. of the following pairs of elements.

(i) Na and K
(ii) Mg and A*l*
(iii) Si and P
(iv) P and S