

DP IB Chemistry: HL


Your notes

3.1 The Periodic Table & Periodic Trends

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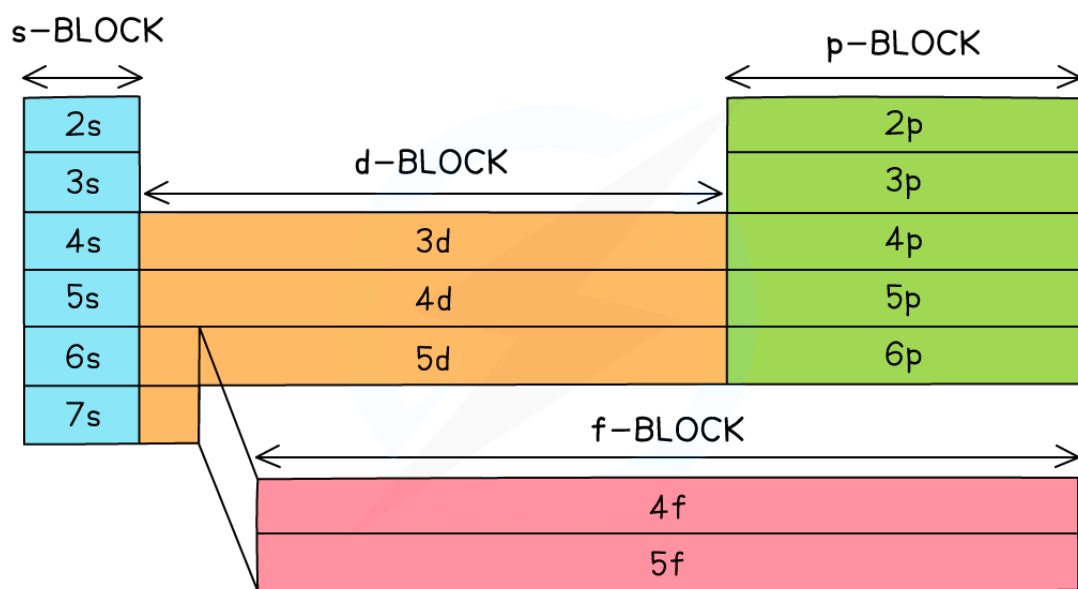


Your notes

3.1.1 The Periodic Table

Structure of the Periodic Table

- The **periodic table** is a list of all known elements arranged in order of **increasing atomic number**, from 1 to 118.
- In addition to this, the elements are arranged in such a way that atoms with the same number of shells are placed together, and atoms with similar electronic configurations in the outer shell are also placed together. This is achieved as follows:
 - The elements are arranged in rows and columns.
 - Elements with **one** shell are placed in the **first row** (i.e. H and He)
 - Elements with **two** shells are placed in the **second row** (Li to Ne) and so on.
- A row of elements thus arranged is called a **period**. The period number, **n**, is the outer energy level that is occupied by electrons.
- In addition, the elements are aligned vertically (in columns) with other elements in different rows, if they share a similar outer-shell electronic configuration
 - The outer electrons are known as the **valence** electrons.
- A column of elements thus arranged is called a **group**



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The blocks of the periodic table

- All elements belong to one of **four** main blocks: the s-block, the p-block, the d-block and the f-block
 - The **s-block** elements are all those with only **s** electrons in the outer shell
 - The **p-block** elements are all those with at least one **p**-electron in the outer shell
 - The **d-block** elements are all those with at least one **d**-electron and at least one **s**-electron but no **f** or **p** electrons in the outer shell (up to 5d)
 - The **f-block** elements are all those with at least one **f**-electron and at least one **s**-electron but no **d** or **p** electrons in the outer shell
- The physical and chemical properties of elements in the periodic table show clear patterns related to the position of each element in the table
 - Elements in the same group show similar properties, and properties change gradually as you go across a period
- As atomic number increases, the properties of the elements show trends which repeat themselves in each period of the periodic table
 - These trends are known as **periodic trends** and the study of these trends is known as **periodicity**



Your notes

Deducing Electron Configurations

- The electron configuration of any element can be deduced from its position in the periodic table
- It is like an 'address' that tells you exactly where an element is found
- Using the element germanium as an example to illustrate how it works:

GROUP 4 TELLS YOU THERE ARE
4 VALENCE ELECTRONS AND PERIOD 4
TELLS YOU THEY ARE IN THE 4th SHELL

(FULL INNER SHELLS) + $4s^2 4p^2$

THE SECOND ELEMENT IN THE p-BLOCK
TELLS YOU TWO ELECTRONS IN THE
p-SUBSHELL

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Deducing the electron configuration of germanium

- Germanium is in **p block**, in **group 4** (using the simplified numbering system) and the **second** element across in **period 4**
- Group 4 tells you there are **four valence electrons** and period 4 tells you the **valence electrons** are in the **fourth shell**
- The **second** position in **p block** tells you that two electrons are in the **p subshell**
- Similarly, you can deduce the position of an element in the periodic table from its electron configuration:

ADD THESE NUMBERS TO
GIVE YOU THE GROUP

$$2 + 5 = 7$$

$1s^2 2s^2 2p^6 3s^2 3p^5$

GROUP 7, THIRD PERIOD,
MEANS IT IS CHLORINE

THIS NUMBER TELLS YOU
THE PERIOD NUMBER WHICH
IS THE OUTER ENERGY LEVEL (n)

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Deducing information from the electron configuration of chlorine

- Test your understanding in the following example:

Worked example

Element Z is in period 4 and group 5 of the periodic table. Which statement is correct?

- A. Z has 5 occupied energy levels.
- B. Z can form ions with 3- charge.
- C. Z is a transition element.
- D. Z has 4 valence electrons.

Answer:

- The correct option is **B**. A group 5 element could form a 3- ion
- It cannot be **A** because 5 occupied energy levels would place it in period 5
- Transition elements would not be found in group 5, so **C** is also incorrect
- 4 valence electrons would match an element in group 4, so **D** must be wrong



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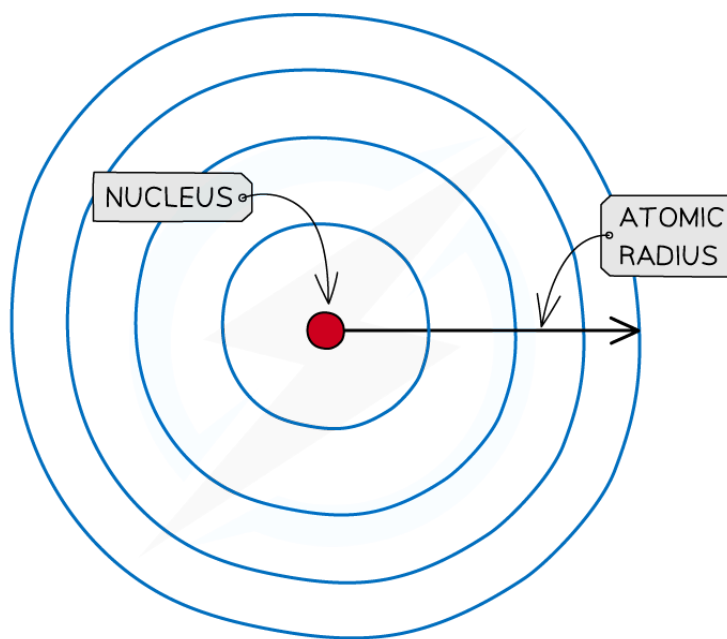
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3.1.2 Periodic Trends: Physical – Atomic & Ionic Radius

Atomic & Ionic Radius

Atomic radius

- The **atomic radius** of an element is a measure of the size of an atom
- It is the distance between the **nucleus** of an atom and the outermost electron shell
- It can be quite hard to determine exactly where the boundary of an atom lies, so a variety of approaches are taken such as half the mean distance between two adjacent atoms
- This will vary depending on the type of structure and bonding, but it gives a comparative value for atoms



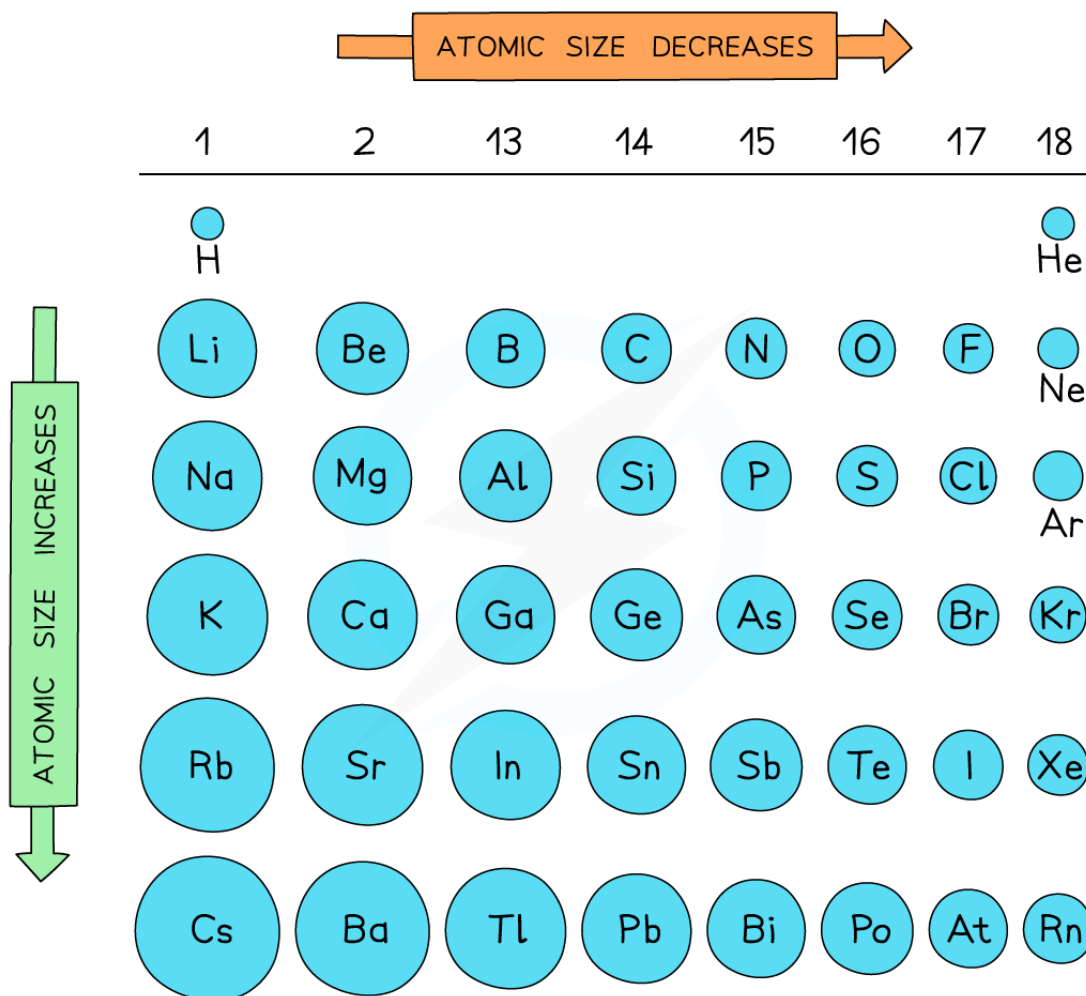
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The atomic radius of an atom is the typical distance between the nucleus and the outermost electron shell

- Atomic radii show predictable patterns across the periodic table
 - They generally **decrease** across each period
 - They generally **increase** down each group
- These trends can be explained by the **electron shell theory**
 - Atomic radii decrease as you move across a period as the atomic number increases (increased positive **nuclear charge**) but at the same time extra electrons are added to the same **principal**

quantum shell

- The larger the nuclear charge, the greater the pull of the nuclei on the electrons which results in smaller atoms
- Atomic radii increase moving down a group as there is an increased number of shells going down the group
- The electrons in the **inner shells** repel the electrons in the **outermost shells**, **shielding** them from the positive nuclear charge
- This weakens the pull of the nuclei on the electrons resulting in larger atoms



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Trends in the atomic radii across a period and down a group

- The diagram shows that the atomic radius increases sharply between the **noble gas** at the end of each period and the **alkali metal** at the beginning of the next period

- This is because the **alkali metals** at the beginning of the next period have **one** extra principal quantum shell
 - This increases shielding of the outermost electrons and therefore increases the atomic radius






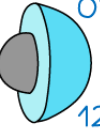
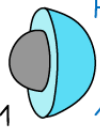



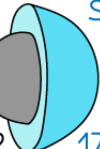











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Ionic radius

- The **ionic radius** of an element is a measure of the size of an ion
- Ionic radii show predictable patterns
 - The trend down a group is the same as atomic radius - it increases as the number of shells increases
 - The trend across a period is not so straightforward as it depends on whether it is positive or negative ions being considered
 - Ionic radii **increase** with increasing **negative charge**
 - Ionic radii **decrease** with increasing **positive charge**
- These trends can also be explained by the **electron shell theory**
 - Ions with **negative** charges are formed by atoms **accepting** extra electrons while the **nuclear charge** remains the same
 - The extra electrons experience repulsion with the other valence electrons which increases the ionic radius
 - The greater the negative charge, the larger the ionic radius
 - **Positively** charged ions are formed by atoms **losing** electrons
 - The **nuclear charge** remains the same but there are now fewer electrons which undergo a **greater electrostatic force of attraction** towards the nucleus which decreases the ionic radius
 - The greater the positive charge, the smaller the ionic radius

SIZES OF ATOMS AND THEIR IONS IN PM

GROUP 1 GROUP 2 GROUP 13 GROUP 16 GROUP 17

PERIOD 2	Li^+ Li  90 134	Be^{2+} Be  59 90	B^{3+} B  41 82	O O^{2-}  73 126	F F^-  71 119
PERIOD 3	Na^+ Na  116 154	Mg^{2+} Mg  86 130	Al^{3+} Al  68 118	S S^{2-}  102 170	Cl Cl^-  99 167
PERIOD 4	K^+ K  152 196	Ca^{2+} Ca  114 174	Ga^{3+} Ga  76 126	Se Se^{2-}  116 184	Br Br^-  114 182
PERIOD 5	Rb^+ Rb  166 211	Sr^{2+} Sr  132 192	In^{3+} In  94 144	Te Te^{2-}  135 207	I I^-  133 206

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Trends in the ionic radii across a period and down a group

 **Worked example**

Which option shows atoms in order of decreasing atomic radius?

- A. $N > C > Be > Mg$
- B. $Mg > N > C > Be$
- C. $Be > C > N > Mg$
- D. $Mg > Be > C > N$

Answer:

Option **D** is the correct answer

- First, you need to identify that Be, C and N are all in period 2, but Mg is in period 3, so Mg will have the biggest radius.
- Secondly, atomic radius decreases across the period so Be, C and N decrease in that order as they belong to groups 2, 14 and 15, respectively



Your notes

3.1.3 Periodic Trends: Physical – Ionisation Energy



Your notes

First Ionisation Energy

- The **ionisation energy** (IE) of an element is the amount of energy required to remove **one mole** of electrons from **one mole** of atoms of an element in the gaseous state to form **one mole** of gaseous ions
- Ionisation energies are measured under **standard conditions** which are 298 K and 100 kPa
- The units of IE are **kilojoules per mole** (kJ mol^{-1})
- The **first ionisation energy** is the energy required to remove the one mole of electrons from one mole the gaseous atoms
 - E.g. the first ionisation energy of calcium:

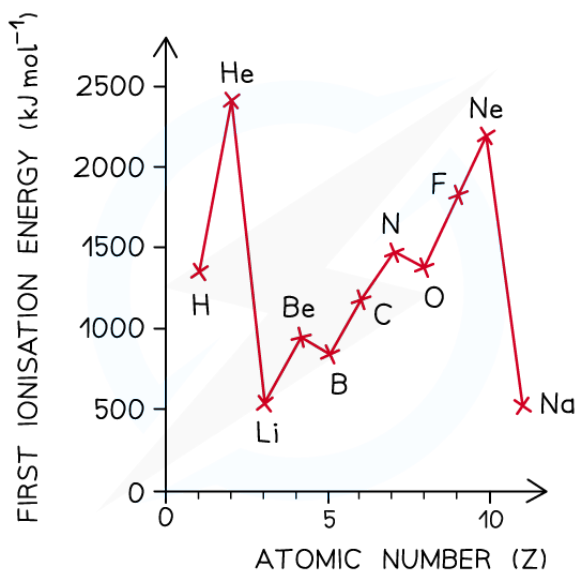




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Ionisation Energies: Trends

- Ionisation energies show **periodicity**
- As could be expected from their electronic configuration, the group I metals show low IE whereas the noble gases have very high IEs
- The **first ionisation** energy **increases** across a period and **decreases** down a group and is caused by **four factors** that influence the ionisation energy:
 - Size of the nuclear charge:** the nuclear charge increases with increasing atomic number, which means that there are greater **attractive forces** between the nucleus and outer electrons, so more energy is required to overcome these attractive forces when removing an electron
 - Distance of outer electrons from the nucleus:** electrons in shells that are further away from the nucleus are less attracted to the nucleus so the further the outer electron shell is from the nucleus, the **lower** the ionisation energy
 - Shielding effect of inner electrons:** the **shielding effect** is when the electrons in full inner shells repel electrons in outer shells preventing them to feel the **full nuclear charge** so the greater the shielding of outer electrons by inner electron shells, the lower the ionisation energy
 - Spin-pair repulsion:** paired electrons in the same atomic orbital in a subshell repel each other more than electrons in different atomic orbitals; this makes it easier to remove an electron (which is why the first ionization energy is always the lowest)



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A graph showing the ionisation energies of the elements hydrogen to sodium

Ionisation energy across a period



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- The ionisation energy across a period increases due to the following factors:
 - Across a period the **nuclear charge** increases
 - The **distance** between the nucleus and outer electron remains reasonably **constant**
 - The **shielding** by inner shell electrons remains the same
- There is a rapid **decrease** in ionisation energy between the **last** element in one period and the **first** element in the next period caused by:
 - The increased **distance** between the nucleus and the outer electrons
 - The increased **shielding** by inner electrons
 - These two factors outweigh the increased **nuclear charge**
- There is a slight **decrease** in 1st I.E. between **beryllium** and **boron** as the fifth electron in boron is in the 2p subshell which is further away from the nucleus than the 2s subshell of beryllium
 - **Beryllium** has a first ionisation energy of **900 kJ mol⁻¹** as its electron configuration is **1s² 2s²**
 - **Boron** has a first ionisation energy of **801 kJ mol⁻¹** as its electron configuration is **1s² 2s² 2p¹**
- There is a slight **decrease** in 1st I.E. between **nitrogen** and **oxygen** due to **spin-pair repulsion** in the 2p subshell of oxygen
 - **Nitrogen** has a first ionisation energy of **1402 kJ mol⁻¹** as its electron configuration is **1s² 2s² 2p³**
 - **Oxygen** has a first ionisation energy of **1314 kJ mol⁻¹** as its electron configuration is **1s² 2s² 2p⁴**

Ionisation energy down a group

- Although going down a group the **nuclear charge** increases, the ionisation energy down a group decreases and it is due to the following factors:
 - The **distance** between the nucleus and outer electron **increases**
 - The **shielding** by inner shell electrons **increases**
 - The **effective nuclear charge** is decreasing as **shielding** increases

Ionisation Energy Trends across a Period & going down a Group Table



Your notes

Across a Period: Ionisation Energy Increases	Down a Group: Ionisation Energy Decreases
Increase in nuclear charge	Increase in nuclear charge
Shell number is the same Distance of outer electron to nucleus is the same	Increase in shells Distance of outer electron to nucleus increases Shielding effect increases, therefore, the attraction of valence electrons to the nucleus decreases
Shielding remains reasonably constant	Increased shielding
Decreased atomic/ionic radius	Increased atomic/ionic radius
The outer electron is held more tightly to the nucleus so it gets harder to remove it	The outer electron is held more loosely to the nucleus so it gets easier to remove it

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Successive ionisation energies of an element

- The **successive** ionisation energies of an element **increase** as removing an electron from a **positive** ion is more difficult than from a **neutral** atom
- As more electrons are removed the attractive forces increase due to **decreasing shielding** and an increase in the proton to electron ratio
- The increase in ionisation energy, however, is not constant and is dependent on the atom's electronic configuration
- Taking calcium as an example:

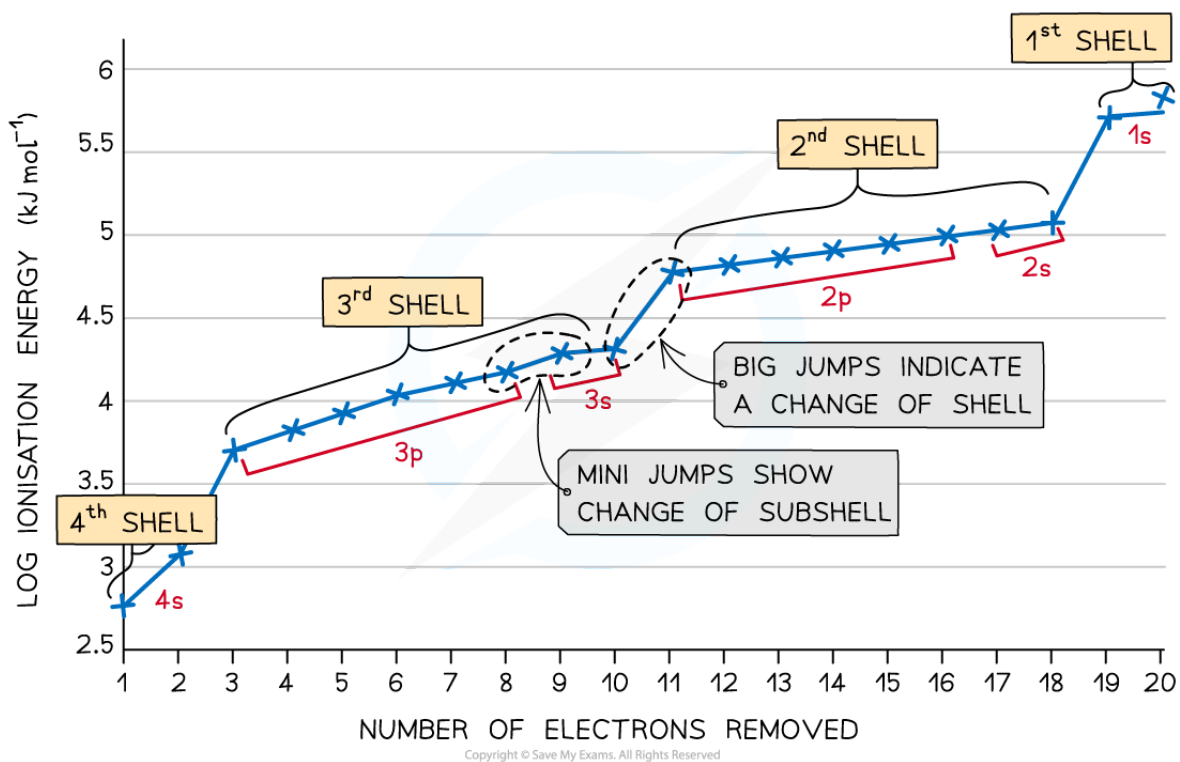
Ionisation Energies of Calcium Table



Electronic Configuration	$1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2$	$1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^1$	$1s^2 2s^2 2p^6$ $3s^2 3p^6$	$1s^2 2s^2 2p^6$ $3s^2 3p^5$
IE	First	Second	Third	Fourth
IE (kJ mol^{-1})	590	1150	4940	6480

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- The values become very large and difficult to represent meaningfully, so it is more convenient to show the logarithm of the ionisation energies
- This helps us to see significant jumps in I.E.



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Successive ionisation energies for the element calcium

- The **first** electron removed has a low ionisation energy as it is easily removed from the atom due to the spin-pair repulsion of the electrons in the 4s orbital

- The **second** electron is a little more difficult to remove than the first electron as you are removing an electron from a positively charged ion
- The **third** electron is much more difficult to remove than the second one corresponding to the fact that the third electron is in a **principal quantum** shell which is closer to the nucleus (3p)
- The graph shows there is a large increase in successive ionisation energy as the electrons are being removed from an increasingly positive ion
- The big jumps on the graph show the change of **shell** and the small jumps are the change of **subshell**

Examiner Tip

Be careful with how you interpret successive ionisation energy graphs as it is common for students to read them the wrong way around and count outer electrons from right to left instead of left to right so they get the jumps in the wrong place. This happens particularly when you are given only a partial successive ionisation energy graph and have to deduce which group the element comes from. It's a good idea if you see an ionisation energy graph in an exam question to label the shells and subshells so you are less likely to make this mistake!



Your notes



Your notes

3.1.4 Periodic Trends: Physical – Electron Affinity

Electron Affinity

- When atoms gain electrons they become negative ions or **anions**
- Electron affinity (EA)** can be thought of as the opposite process of ionisation energy and is defined as
 - The amount of energy released when **one mole** of electrons is gained by **one mole** of atoms of an element in the gaseous state to form **one mole** of gaseous ions
- Electron affinities are measured under **standard conditions** which are 298 K and 100 kPa
- The units of EA are **kilojoules per mole** (kJ mol^{-1})
- The **first electron affinity** is always exothermic
 - E.g. the first electron affinity of chlorine is:

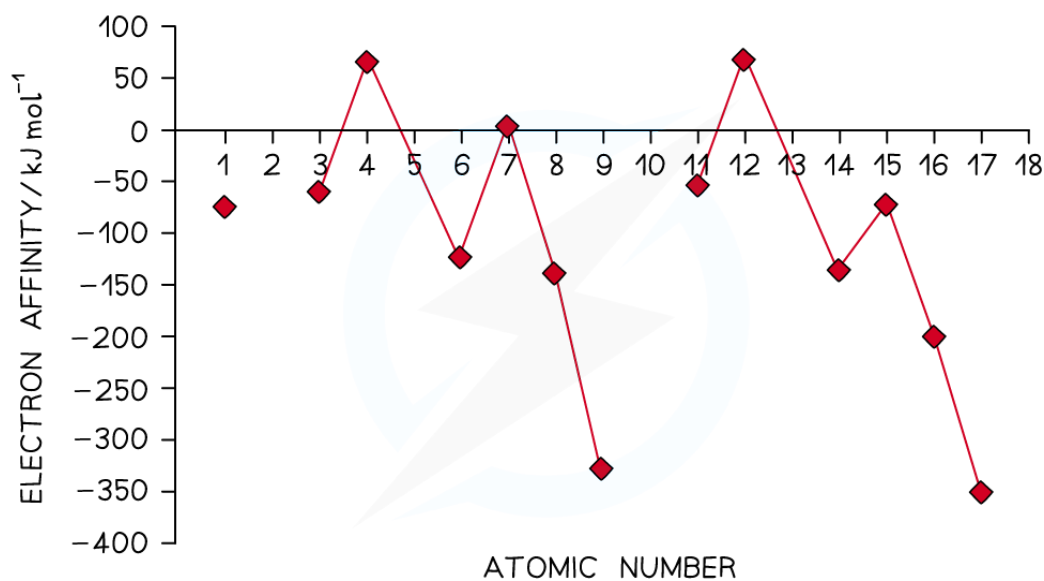


- However, the second electron affinity can be an endothermic process



- This is due to the fact that you are overcoming repulsion between the electron and a negative ion, so energy is required making the process endothermic overall

Trends in electron affinity

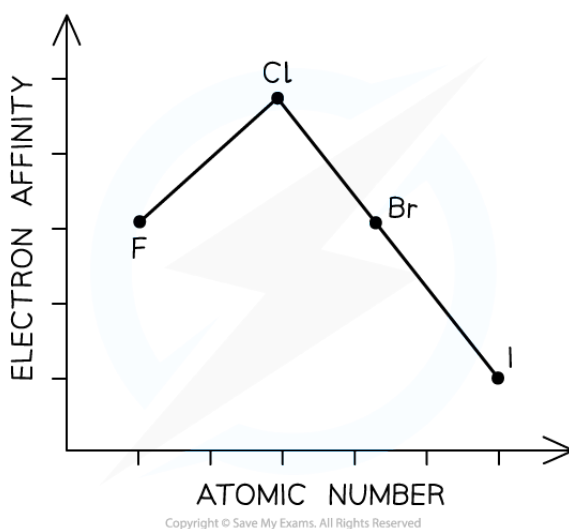


Electron affinities across a period



Your notes

- Electron affinities show **periodicity**
- The pattern is very similar to ionisation energies, except that it is inverted and the minimum points are displaced one element to the right
- As might be expected, the most exothermic electron affinities are for group 17 elements which also have the highest electronegativities
- The strongest pull on electrons correlates with the greater amount of energy released when negative ions are formed
- Noble gases do not form negative ions, so they don't appear in this chart
- The electron affinities reach a peak for group 2 and group 5 elements



Electron affinities down a group

- **Electron affinities** generally decrease down a group
- As the atoms become larger the attraction for an additional electron is less, since the **effective nuclear charge** is reduced due to increased **shielding**
- Electron affinity become **less exothermic** going down the group
- An exception to this is fluorine whose **electron affinity** is smaller than expected
- This is because fluorine is such a small atom and an additional electron in the 2p subshell experiences considerable repulsion with the other valence electrons

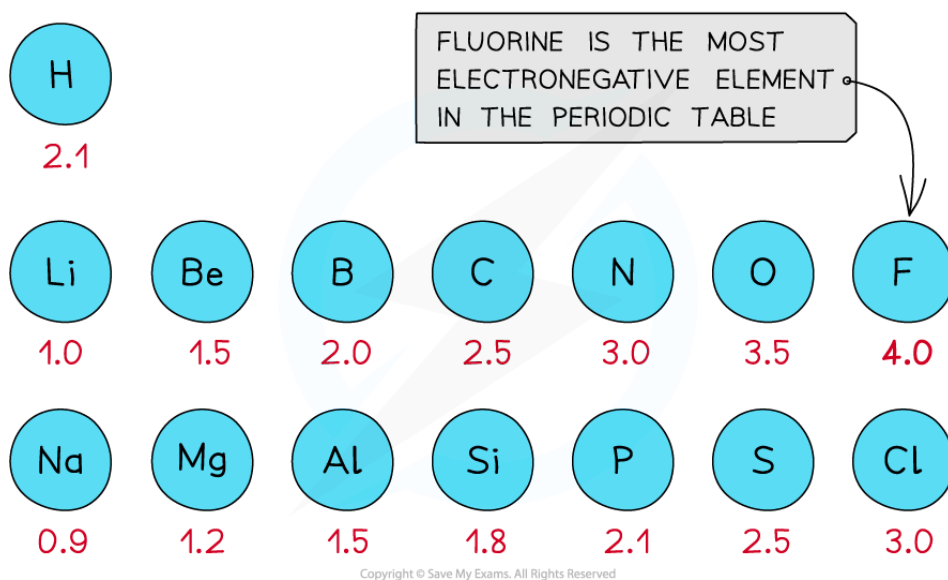


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3.1.5 Periodic Trends: Physical – Electronegativity

Electronegativity: Definition

- **Electronegativity** is the ability of an atom to attract a pair of electrons towards itself in a covalent bond
- This phenomenon arises from the **positive** nucleus's ability to attract the **negatively** charged electrons, in the outer shells, towards itself
- The **Pauling scale** is used to assign a value of electronegativity for each atom

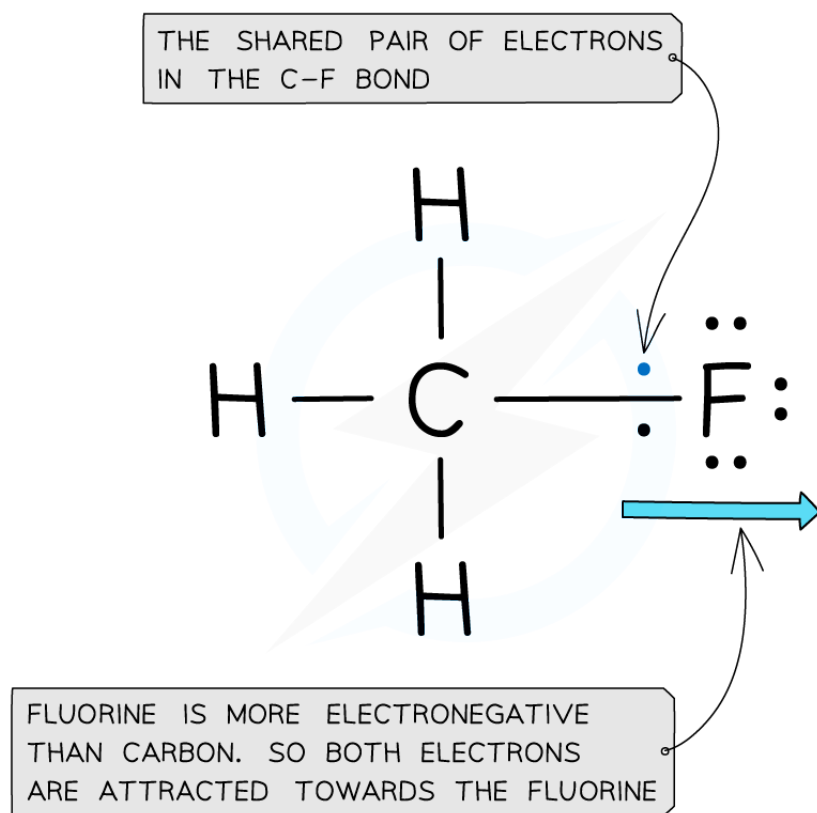


First three rows of the periodic table showing electronegativity values

- Fluorine is the most electronegative atom on the Periodic Table, with a value of 4.0 on the **Pauling Scale**
- It is best at attracting electron density towards itself when covalently bonded to another atom



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Electron distribution in the C-F bond of fluoromethane



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Electronegativity: Affecting Factors

Nuclear charge

- **Attraction** exists between the positively charged **protons** in the nucleus and negatively charged **electrons** found in the energy levels of an atom
- An **increase** in the number of **protons** leads to an **increase** in **nuclear attraction** for the electrons in the outer shells
- Therefore, an **increased nuclear charge** results in an **increased electronegativity**

	Na	Mg	Al
NUMBER OF PROTONS:	11	12	13
ELECTRONEGATIVITY:	0.9	1.2	1.5

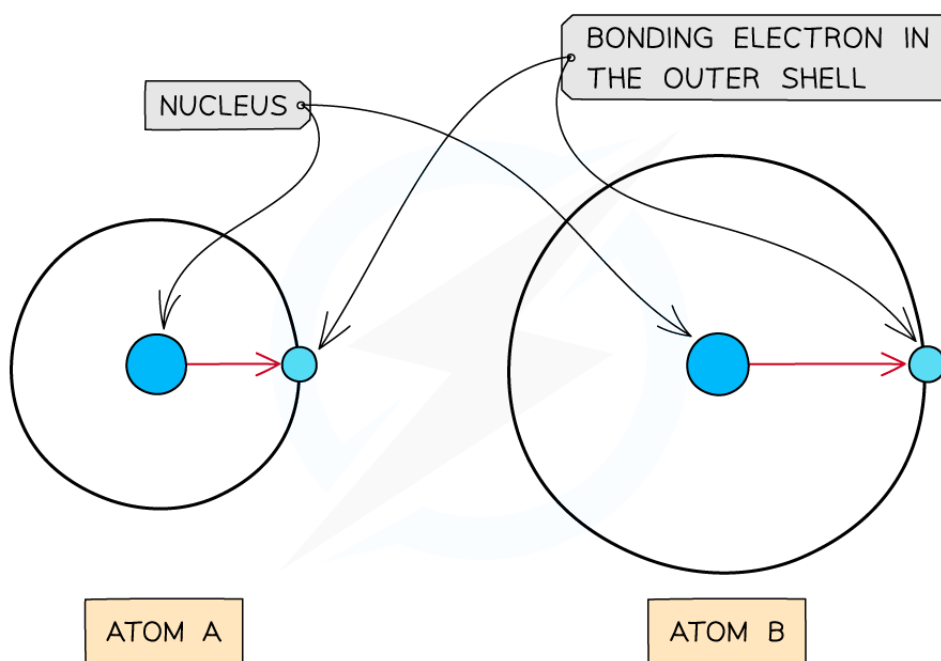
AS THE NUMBER OF PROTONS INCREASE,
THE ELECTRONEGATIVITY INCREASES

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As the nuclear charge increases, the electronegativity of an element increases as well

Atomic radius

- The **atomic radius** is the distance between the nucleus and electrons in the **outermost shell**
- Electrons **closer** to the nucleus are more **strongly** attracted towards its positive **nucleus**
- Those electrons **further away** from the nucleus are **less strongly** attracted towards the **nucleus**
- Therefore, an **increased atomic radius** results in a **decreased electronegativity**



As the atomic radius increases, the nucleus has less of an attraction for the bonding electrons causing atom A to have a higher electronegativity than atom B



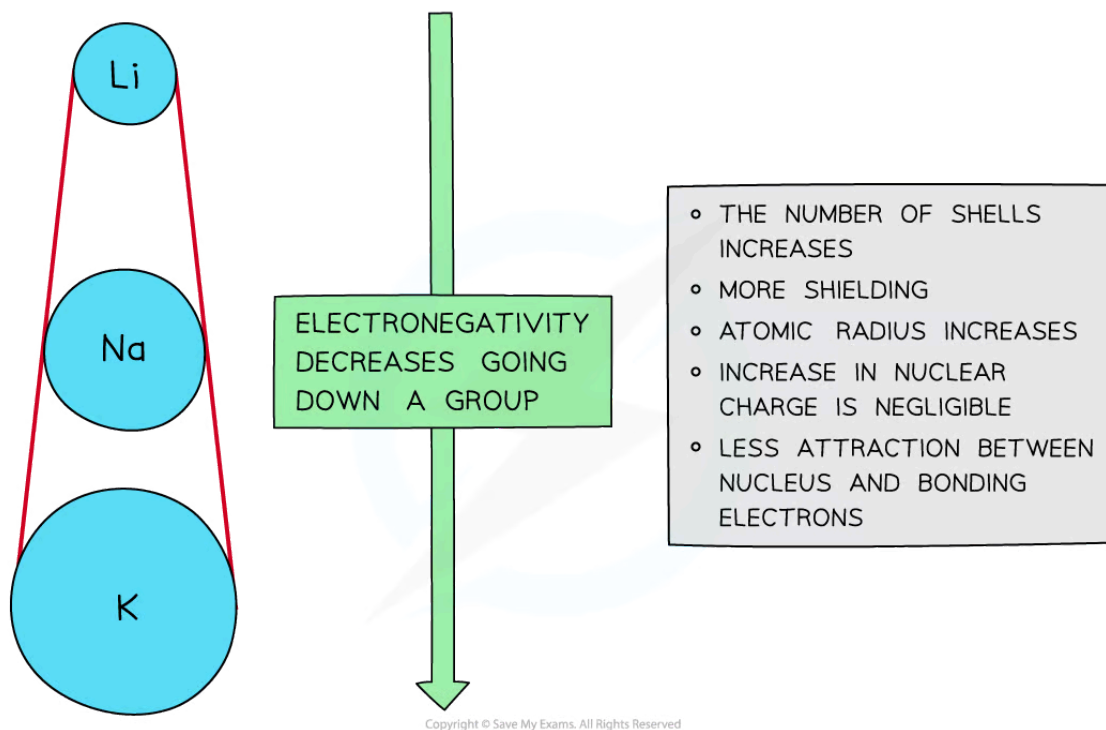
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Electronegativity: Trends

- **Electronegativity** varies across periods and down the groups of the periodic table

Down a group

- There is a **decrease** in **electronegativity** going down the group
- The **nuclear charge increases** as more protons are being added to the nucleus
- However, each element has an extra filled electron shell, which increases **shielding**
- The addition of the extra shells increases the distance between the nucleus and the outer electrons resulting in **larger atomic radii**
- Overall, there is decrease in attraction between the nucleus and outer bonding electrons
- We say the **effective nuclear charge** has decreased down the group



Electronegativity decreases going down the groups of the periodic table

Across a period

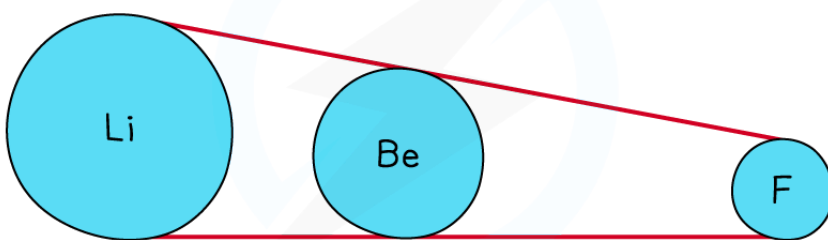
- Electronegativity **increases** across a period
- The **nuclear charge increases** with the addition of protons to the nucleus
- **Shielding** remains the **same** across the period as no new shells are being added to the atoms



Your notes

- The nucleus has an increasingly strong attraction for the bonding pair of electrons of atoms across the period
- This results in **smaller atomic radii**

◦ NUCLEAR CHARGE INCREASES
 ◦ ATOMIC RADIUS DECREASES
 ◦ GREATER ATTRACTION BETWEEN NUCLEUS AND OUTER ELECTRONS



ELECTRONEGATIVITY INCREASES GOING ACROSS A PERIOD

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Electronegativity increases going across the periods of the periodic table

Trends down a Group & across a Period Table

	Down a Group	Across a Period
Nuclear charge	Increases	Increases
Shielding	Increases	Reasonably constant
Atomic radius	Increases	Decreases
Electronegativity	Decreases	Increases

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 **Examiner Tip**

Make sure you learn the definition of **electronegativity** and can distinguish it from **electron affinity** as the two are often confused. **Electronegativity** is about chemical character and only applies to considerations of covalent bonds whereas **electron affinity** is a thermodynamic value that is measurable and applies to the formation of negative ions. You may come across something called **electropositivity** - this is a term used to describe the character of elements to form positive ions and is useful when talking about metal atoms and metal ions



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3.1.6 Periodic Trends: Chemical

Metallic & Non-metallic

- Periodic trends can also be seen in the typical properties of metals and non-metals which are summarised below:

Property	Metals	Non-metals
Electron arrangement	1–3 (more in Periods 5 & 6) outer shell electrons	4–7 electrons in the outer shell
Bonding	Metallic due to loss of outer shell electrons	Covalent by sharing of outer shell electrons
Electrical conductivity	Good conductors of electricity	Poor conductors of electricity
Type of oxide	Basic oxides (a few are amphoteric)	Acidic oxides (some are neutral)
Reaction with acids	Many react with acids	Do not react with acids
Physical characteristics	Malleable, can be bent and shaped High melting and boiling point	Flaky, brittle Low melting and boiling point

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The typical properties of metals and non-metals

- The typically properties of metals and non-metals can be explained by reference to their trends in atomic radius, ionic radius, ionisation energy, electron affinity and electronegativity
- The low **ionisation energies** and low **electronegativities** of metals can account for the ability of their **valence electrons** to move away from the nucleus
 - This is known as '**delocalisation**' of the electrons
- These properties increase from left to right as you transition from metal to metalloid to non-metal
- The high **electronegativity** and **electron affinity** of non-metals can be related to their tendency to share electrons and form covalent bonds, either with themselves or other non-metal elements
- The similarities in **electronegativities** of the diagonal band of **metalloids** which divides the metals from the non-metals explains the behaviour of **metalloids**

Test yourself on the trends in the periodic table:



Your notes

Worked example

Which increase across a period from left to right?

A	Ionic radius	Electronegativity
B	Atomic radius	Ionic radius
C	1st ionization energy	Atomic radius
D	1st ionization energy	Electronegativity

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Answer:

The correct option is **D**

- Across a period atomic radius decreases, electronegativity and ionisation energy increase and ionic radius increases then decreases