

CHAPTER 3: Electrons in Atoms

3.1 Sub-shells and Atomic Orbitals

3.2 Electronic Configuration

3.3 Ionisation Energy

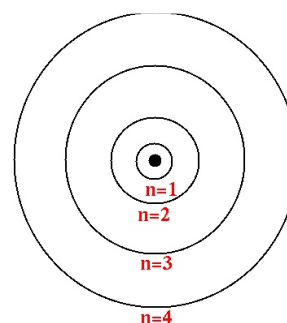
Learning outcomes:

- (a) describe the number and relative energies of the s , p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the $4s$ and $4p$ orbitals.
- (b) describe the shapes of s and p orbitals.
- (c) state the electronic configuration of atoms and ions given the proton number (and charge), using the convention $1s^2 2s^2 2p^6$ etc.
- (d)
 - (i) explain and use the term ionisation energy.
 - (ii) explain the factors influencing the ionisation energies of elements.
 - (iii) explain the trends in ionisation energies across a Period and down a Group of the Periodic Table.
- (e) deduce the electronic configurations of elements from successive ionisation energy data.
- (f) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table.

3.1 Sub-shells and Atomic Orbitals

Principle quantum shell

- 1) Electrons are arranged outside the nucleus in **energy levels** or **principle quantum shell, n**.
- 2) The principal quantum shells are numbered according to how far they are from the nucleus.
- 3) The lowest energy level, $n = 1$ is closest to the nucleus, the energy level $n = 2$ is further out, and so on.
- 4) The electrons in energy level further away from the nucleus have more energy and are held less tightly by the nucleus.
- 5) Electrons **do not** move in fixed circular paths, they occupy a space called the atomic orbitals.
- 6) The total number of electrons that can occupy any principal shell is $2n^2$, where n is the principal quantum number.

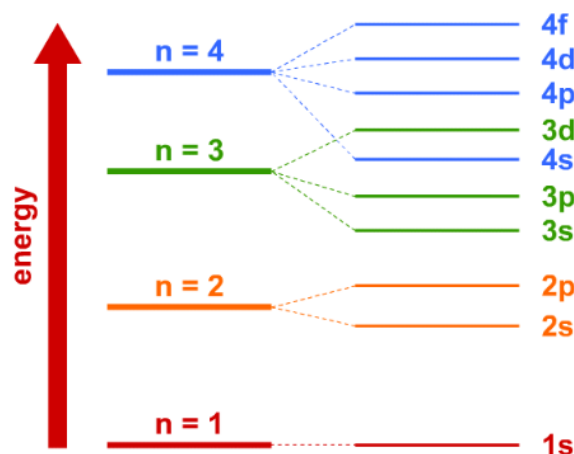


The circles represent energy levels

Quantum sub-shells

- 1) The principal quantum shells, apart from the first, are split into sub-shells. Each principal quantum shell contains a different number of sub-shells.
- 2) The first energy level contains one sub-shell, the second energy level contains two and so on.
- 3) The sub-shells are distinguished by letters s, p, d, f and so on.
- 4) The energy of electrons in the sub-shells increases in the order $s < p < d < f$.

Principal quantum shell	Maximum number of electrons	Number of sub-shells	Name of sub-shells
K, $n = 1$	2	1	1s
L, $n = 2$	8	2	2s, 2p
M, $n = 3$	18	3	3s, 3p, 3d
N, $n = 4$	32	4	4s, 4p, 4d, 4f



The impossibility of drawing orbits for electrons

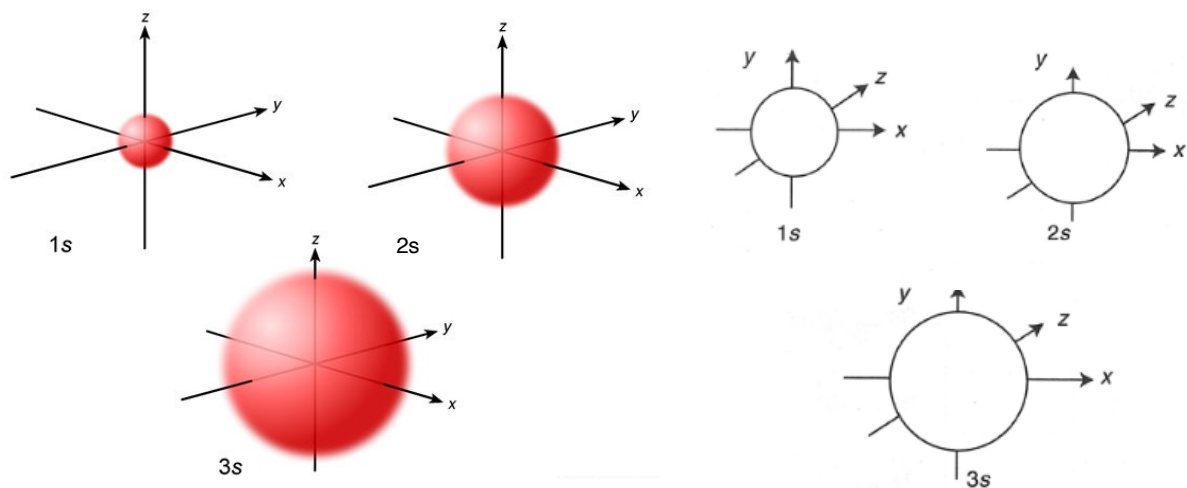
- 1) Heisenberg Uncertainty Principle says, you cannot know with certainty where an electron is and where it is going next.
- 2) This makes it impossible to draw out an orbit or pathway in which the electrons move.

Atomic orbitals

- 1) An *atomic orbital* is a region of space around the nucleus where the probability of finding a particular electron is maximum (>95%).
- 2) The sub-shells are split further into orbitals where the electrons are placed.

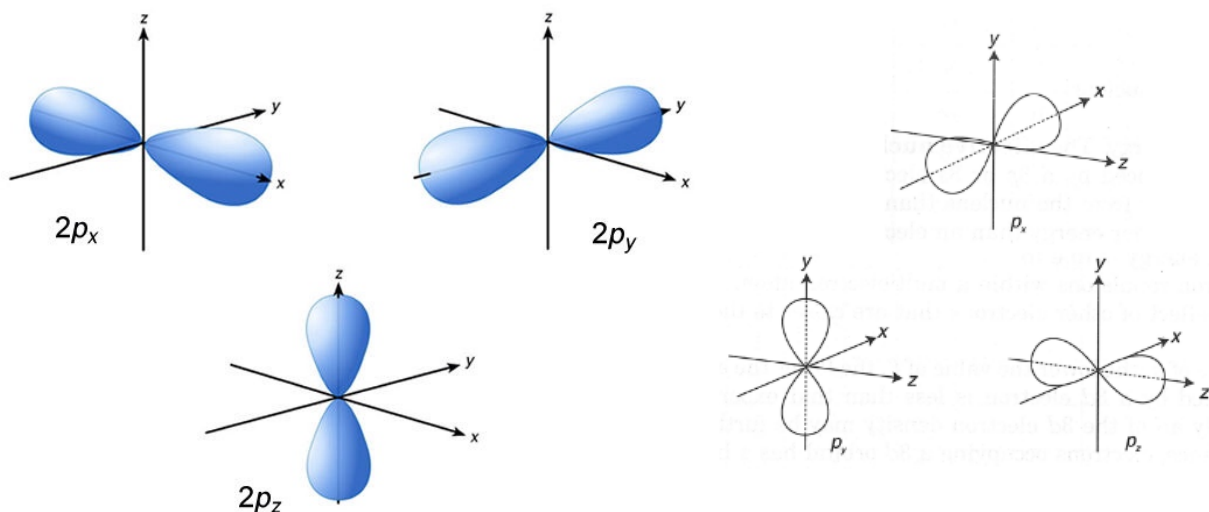
- 3) The number of orbital in each sub-shell depends on the sub-shells.
s - one orbital {s}
p - three orbitals {p_x, p_y, p_z}
d - five orbitals {d_{xy}, d_{yz}, d_{xz}, d_{x²-y²}, d_{z²}}
- 4) Orbitals having the same energy are called degenerate orbitals. For example, p_x, p_y and p_z are degenerate orbitals.
- 5) The concept of orbitals arises from the fact that an electron has dual nature. It behaves as a particle as well as a wave.
- 6) In the **nth** principal quantum shell, there are **n** sub-shells, **n²** orbitals and a maximum of **2n²** electrons.

The s orbital

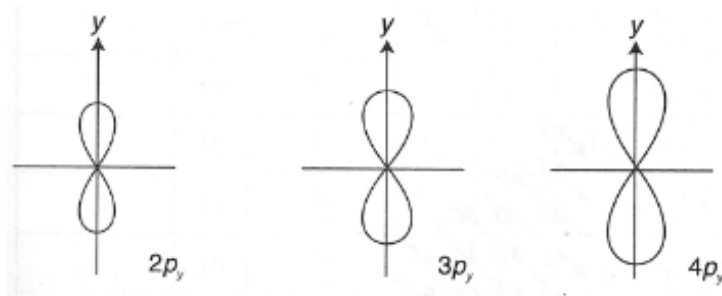
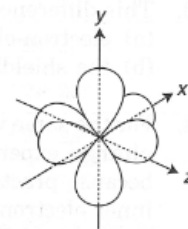


- 1) All the s orbitals are **spherical** and **non-directional**.
- 2) The shaded region represents the region in which the chance of finding the s electron is more than 95%.
- 3) The size of the s orbital increases in the order $1s < 2s < 3s < 4s$.

The p orbital



- 1) All the p orbitals are **dumb-bell shaped** and **directional**.
- 2) p orbitals are only available from the second principal quantum shell and onwards.
- 3) There are 3 types of p orbitals, p_x , p_y and p_z . All 3 different types of p orbitals are perpendicular to each other along the x, y and z axes.
- 4) Going to a higher energy level, the 'lobes' of the p orbital become longer.



3.2 Electronic Configuration

Ways to represent electronic configuration

Electronic configuration describes how the electrons in an atom/ion are arranged in their shells, sub-shells and orbitals.

1) Using 'electrons-in-boxes':

	1s	2s	2p _x	2p _y	2p _z		1s	2s	2p _x	2p _y	2p _z
B	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow			O	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow
C	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow		F	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow
N	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	Ne	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

2) Using energy levels:

B	2,3	Na	2,8,1
C	2,4	Mg	2,8,2
N	2,5	Al	2,8,3
Ne	2,8	Ar	2,8,8

3) Using s, p, d and f notation:

energy level \rightarrow **1s²** \leftarrow number of electrons in orbital
 \nwarrow type of orbital

or **FULL** electronic configurations:

B	1s ² 2s ² 2p ¹	B	1s ² 2s ² 2p _x ¹ 2p _y ⁰ 2p _z ⁰
C	1s ² 2s ² 2p ²	C	1s ² 2s ² 2p _x ¹ 2p _y ¹ 2p _z ⁰
N	1s ² 2s ² 2p ³	N	1s ² 2s ² 2p _x ¹ 2p _y ¹ 2p _z ¹
O	1s ² 2s ² 2p ⁴	O	1s ² 2s ² 2p _x ² 2p _y ¹ 2p _z ¹
F	1s ² 2s ² 2p ⁵	F	1s ² 2s ² 2p _x ² 2p _y ² 2p _z ¹
Ne	1s ² 2s ² 2p ⁶	Ne	1s ² 2s ² 2p _x ² 2p _y ² 2p _z ²

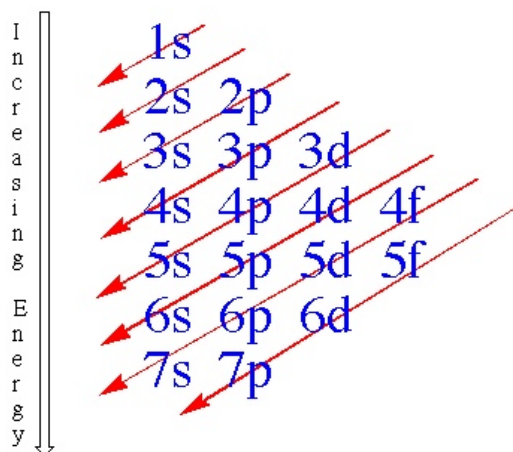
4) Using the noble gas 'core':

B	[He] 2s ² 2p ¹	Na	[Ne] 3s ¹
C	[He] 2s ² 2p ²	Mg	[Ne] 3s ²
N	[He] 2s ² 2p ³	Al	[Ne] 3s ² 3p ¹

Filling in the orbitals

1) Three general rules of filling the orbitals are:

- i. *Aufbau Principle* states that in the ground state of an atom, the electrons must occupy the orbitals in the order of **increasing energy**.

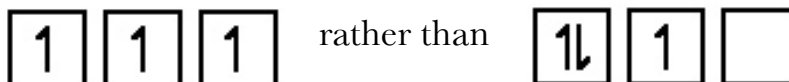


[Note: 4s has a slightly lower energy than 3d, therefore electrons are filled in 4s orbital first before the 3d orbitals.]

- ii. *Pauli's Exclusion Principle* states that an orbital can only accommodate a maximum of **two** electrons only. The two electrons must have opposite spins.



- iii. *Hund's Rule* states that in a set of degenerate orbitals, electrons must occupy the orbital **singly first before pairing**. The reason is because, two electrons occupying the same orbital will experience repulsion.



2) Electronic configuration of the elements (up to $Z = 38$)

<i>Element</i>	<i>Energy Level</i>	<i>s, p, d, f notation</i>	<i>Period No.</i>	<i>Group No.</i>	<i>Remarks</i>
${}_1\text{H}$	1	$1s^1$	1	I	
${}_2\text{He}$	2	$1s^2$	1	II	
${}_3\text{Li}$	2, 1	$1s^2 2s^1$	2	I	
${}_4\text{Be}$	2, 2	$1s^2 2s^2$	2	II	
${}_5\text{B}$	2, 3	$1s^2 2s^2 2p^1$	2	III	
${}_6\text{C}$	2, 4	$1s^2 2s^2 2p^2$	2	IV	
${}_7\text{N}$	2, 5	$1s^2 2s^2 2p^3$	2	V	half-filled 2p-orbitals
${}_8\text{O}$	2, 6	$1s^2 2s^2 2p^4$	2	VI	
${}_9\text{F}$	2, 7	$1s^2 2s^2 2p^5$	2	VII	
${}_{10}\text{Ne}$	2, 8	$1s^2 2s^2 2p^6$	2	0	noble gas
${}_{11}\text{Na}$	2, 8, 1	$1s^2 2s^2 2p^6 3s^1$	3	I	
${}_{12}\text{Mg}$	2, 8, 2	$1s^2 2s^2 2p^6 3s^2$	3	II	
${}_{13}\text{Al}$	2, 8, 3	$1s^2 2s^2 2p^6 3s^2 3p^1$	3	III	
${}_{14}\text{Si}$	2, 8, 4	$1s^2 2s^2 2p^6 3s^2 3p^2$	3	IV	
${}_{15}\text{P}$	2, 8, 5	$1s^2 2s^2 2p^6 3s^2 3p^3$	3	V	half-filled 3p-orbitals
${}_{16}\text{S}$	2, 8, 6	$1s^2 2s^2 2p^6 3s^2 3p^4$	3	VI	
${}_{17}\text{Cl}$	2, 8, 7	$1s^2 2s^2 2p^6 3s^2 3p^5$	3	VII	
${}_{18}\text{Ar}$	2, 8, 8	$1s^2 2s^2 2p^6 3s^2 3p^6$	3	0	noble gas
${}_{19}\text{K}$	2, 8, 8, 1	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	4	I	4s filled first before 3d
${}_{20}\text{Ca}$	2, 8, 8, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	4	II	
${}_{21}\text{Sc}$	2, 8, 9, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	4	TE	
${}_{22}\text{Ti}$	2, 8, 10, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$	4	TE	
${}_{23}\text{V}$	2, 8, 11, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	4	TE	
${}_{24}\text{Cr}$	2, 8, 12, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	4	TE	half-filled 3d & 4s
${}_{25}\text{Mn}$	2, 8, 13, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	4	TE	
${}_{26}\text{Fe}$	2, 8, 14, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	4	TE	
${}_{27}\text{Co}$	2, 8, 15, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$	4	TE	
${}_{28}\text{Ni}$	2, 8, 16, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$	4	TE	
${}_{29}\text{Cu}$	2, 8, 18, 1	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	4	TE	filled 3d & half-filled 4s
${}_{30}\text{Zn}$	2, 8, 18, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	4	TE	
${}_{31}\text{Ga}$	2, 8, 18, 3	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	4	III	
${}_{32}\text{Ge}$	2, 8, 18, 4	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	4	IV	
${}_{33}\text{As}$	2, 8, 18, 5	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	4	V	
${}_{34}\text{Se}$	2, 8, 18, 6	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$	4	VI	
${}_{35}\text{Br}$	2, 8, 18, 7	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	4	VII	
${}_{36}\text{Kr}$	2, 8, 18, 8	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	4	0	noble gas
${}_{37}\text{Rb}$	2, 8, 18, 8, 1	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$	5	I	
${}_{38}\text{Sr}$	2, 8, 18, 8, 2	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	5	II	

3) The odd ones (K, Sc, Cr and Cu):

- i. For potassium, 4s is filled before 3d because 4s has a **lower energy level** than 3d.
- ii. For scandium (to zinc, the d-block elements), the energy level of 3d and 4s are **reversed**. 4s is at a higher energy level now. This is because once the 3d orbital(s) is/are filled, the 3d electrons **repel** the 4s electrons to a higher energy level.
- iii. For chromium, the electronic configuration is $[\text{Ar}]3d^54s^1$ instead of $[\text{Ar}]3d^44s^2$. This is because orbitals that are **fully filled or half filled have extra stability** due to their symmetrical charge distribution.



- iv. For copper, the electronic configuration is $[\text{Ar}]3d^{10}4s^1$ instead of $[\text{Ar}]3d^94s^2$. The reason is the same as stated in (iii).

Electronic configuration of ions

- 1) In the formation of cation, the electrons are removed in the order of decreasing energy (the reverse of filling in).
- 2) For the d-block elements, the electrons in 4s is removed first before 3d. This is because once the 3d orbital is filled, the 4s electrons are repelled to a higher energy level than 3d.
- 3) In the formation of anion, the electrons are added in the same manner as filling the electrons.

Orbitals and the Periodic Table

<i>s-block</i>										<i>p-block</i>										<i>Noble Gas</i>															
I		II				1		2				III		IV		V		VI		VII		0													
3	Li	4	Be			H		He				5	B	6	C	7	N	8	O	9	F	10	Ne												
11	Na	12	Mg									13	Al	14	Si	15	P	16	S	17	Cl	18	Ar												
<i>d-block</i>																																			
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	57	La	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
87	Fr	88	Ra	89	Ac	<i>f-block</i>																													
		58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu						
		90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr						

- 1) The elements in the Periodic Table can be divided into four blocks according to their valence shell electronic configuration.
- 2) The s-block elements have their valence electron(s) in the s orbital.
- 3) The p-block elements have their valence electrons in the p orbital.
- 4) The d-block elements have d orbitals filling.
- 5) The f-block elements have f orbitals filling.

Some useful facts

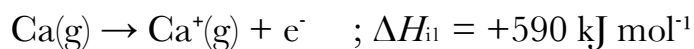
- 1) The valence electrons always appear at the end of the electronic configuration.
(but not necessary the last one).
- 2) The valence electrons are large responsible for the chemical properties of an element.
- 3) The **number of valence electron** will indicate the **group number** of that element in the Periodic Table.
- 4) The **outermost quantum shell number** will indicate the **period** of that element in the Periodic Table.

3.3 Ionisation Energy

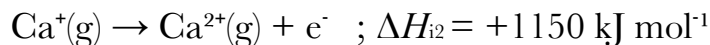
What is ionisation energy?

1) The *1st ionisation energy*, ΔH_{i1} is the energy needed to remove one electron from each atom in one mole of the atoms of the element in the **gaseous state** to form one mole of gaseous $1+$ ions.

2) The general unit for ionisation energy is kJ mol^{-1} .



3) If a second electron is removed from the gaseous $1+$ ions, it is the 2nd ionisation energy, ΔH_{i2} .



4) The *2nd ionisation energy*, ΔH_{i2} is the energy needed to remove one electron from each gaseous $1+$ ion in one mole of the ions to form one mole of gaseous $2+$ ion.

5) The continuous removal of electrons until the nucleus is left only will result in successive ionisation energies.

Factors affecting the ionisation energy

1) **Charge on the nucleus (Number of proton)**

- The greater the number of proton in the nucleus, the greater the amount of positive charge.
- The greater the positive charge, the **greater the attractive force** between the nucleus and outer electrons.
- More energy is needed to overcome the attractive force. So, the ionisation energy is higher.
- **The greater the nuclear charge, the higher the ionisation energy.**

2) Distance between nucleus and outer electrons (Size of atom/ion)

- The larger the size of the atom, the greater the distance between the nucleus and the outer electrons.
- The greater the distance between the nucleus and the outer electrons, the **weaker the attractive force** between nucleus and outer electrons.
- Furthermore, the outer electrons experience greater shielding effect by the inner electrons.
- Less energy is required to overcome the attractive force. So, the ionisation energy is lower.
- **The greater the distance between nucleus and outer electrons, the lower the ionisation energy.**

3) Shielding effect by the inner electrons

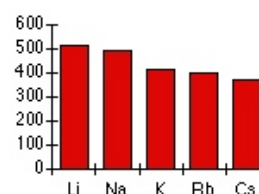
- All electrons are negatively-charged, so they repel each other. Electrons in full inner shells will repel the outer electrons and so prevent the full nuclear charge being felt by the outer electrons. This is called shielding or screening.
- The greater the shielding effect, the **weaker the attractive force** between the nucleus and outer electrons.
- Less energy is required to overcome the attractive force. So, the ionisation energy is lower.
- **The greater the shielding effect, the lower the ionisation energy.**

Pattern of ionisation down a Group

1) The first ionisation energy **decreases** down a Group.

2) This is because the atomic size increases and hence the distance between the nucleus and outer electrons increases. The outer electrons also experience a greater shielding effect.

First ionisation energies (kJ per mole)

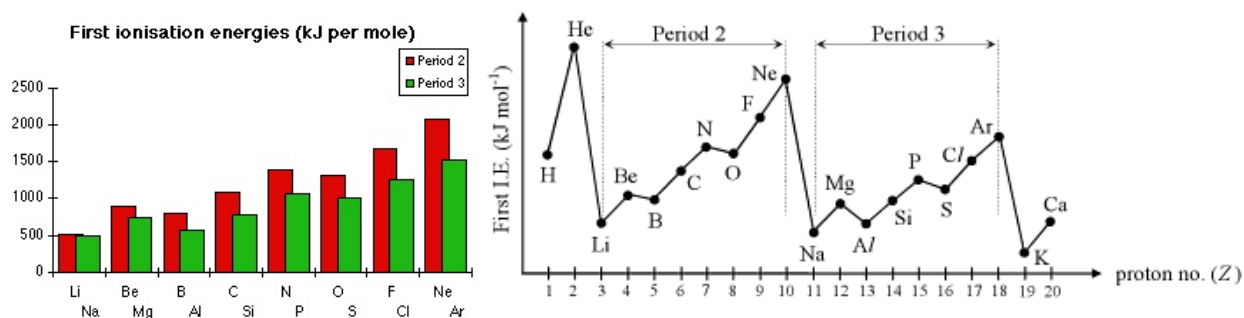


3) These two factors **outweigh** the increasing nuclear charge.

4) The above factors causes the attractive force between nucleus and outer electrons to decrease, less energy is required to overcome the weaker attractive force. Hence, the ionisation energy is lower.

Pattern of ionisation energy across a Period

- 1) The general trend of ionisation energy across a Period is **increasing**.
- 2) This is because, across a Period, the number of proton in the nucleus increases by one therefore the nuclear charge increases.
- 3) However, the distance between the nucleus and outer electrons decreases across a Period and the outer electrons experience the same amount of shielding.
- 4) The above factors causes the attractive force between nucleus and outer electrons to increase, more energy is required to overcome the stronger attractive force. Hence, the ionisation energy is higher.



The drop between (Be-B) and (Mg-Al)

- 1) There is a slight decrease in first ionisation energy between beryllium-boron and magnesium-aluminium.
- 2) This is because the fifth electron in boron is located in the 2p sub-shell, which is slightly further away from the nucleus. The outer electron in boron is shielded by the 1s² as well as 2s² electrons.



- 3) The decrease in first ionisation energy between magnesium and aluminium has the same reason, except that everything is happening at the third energy level.

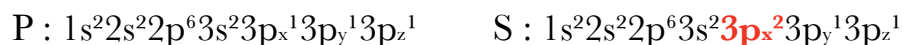


The drop between (N-O) and (P-S)

- 1) There is a slight decrease in first ionisation energy between nitrogen-oxygen and phosphorus-sulphur.
- 2) This is because the electron being removed in oxygen is from the orbital which contains **a pair** of electrons. The extra repulsion between the pair of electrons results in less energy needed to remove the electron. This is called **spin-pair repulsion**.

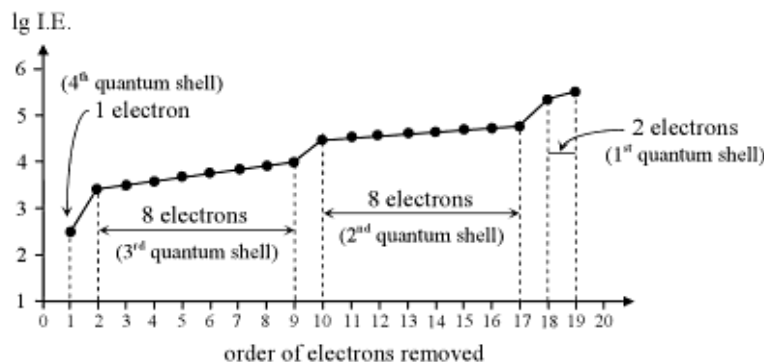


- 3) The decrease in first ionisation energy between phosphorus and sulphur has the same reason, except that everything is happening at the third energy level.

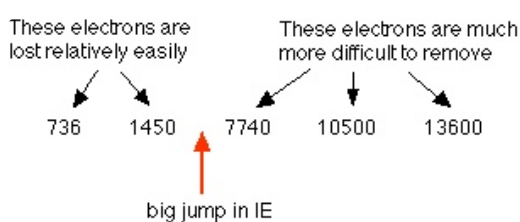


Successive ionisation energy

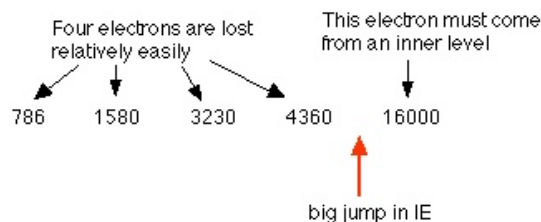
- 1) The following data can be obtained from successive ionisation energy:
 - i. Total number of electrons in an atom.
 - is equal to the number of separate ionisation energies possessed by the atom.
 - ii. Number of principal quantum shells occupied and the number of electrons in each.
 - by looking the big difference between two successive ionisation energies.
 - iii. Number of sub-shells occupied and the number of electrons in each.
- 2) Successive ionisation energies get larger because removing an electron from a positive ion with increasing positive charge is going to be more difficult due to the increasing attractive force.



- 3) There is a relatively big increase in ionisation energy between the first and second electron being removed. This suggests that the second electron being removed is from a principal quantum shell closer to the nucleus.
- 4) The big jump occurs three times, so there are four principal quantum shells occupied by this atom.
- 5) After the big jumps, there is a steady increase in ionisation energy, this suggests that the electrons being removed come from the same principal quantum shell.
- 6) The electronic configuration for this atom can be written as 2,8,8,1.
- 7) Two more examples:

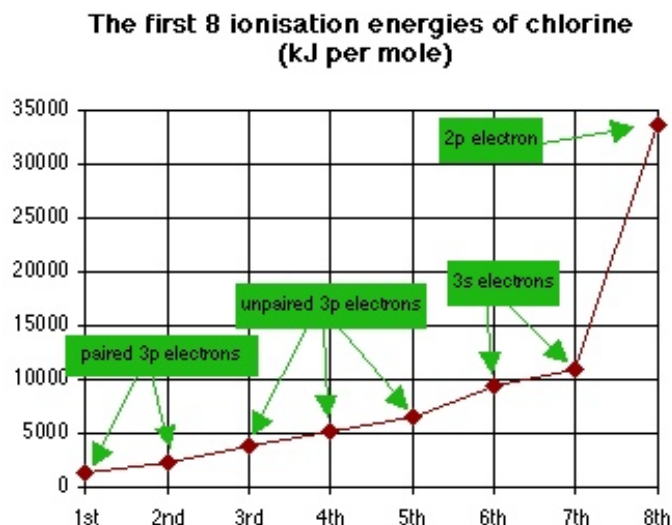


This element comes from Group 2
of the Periodic Table



This element comes from Group 14
of the Periodic Table

Looking at the pattern in more detail



- 1) The electronic configuration of chlorine is $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$.
- 2) Between the second and third ionisation energy, there is a slight increase in difference in ionisation energy. This is because the first two electrons being removed come from the orbitals which contain a paired electrons. The extra repulsion between the electrons result in the ionisation energy being lower.
- 3) There is also a slight increase in difference in ionisation energy between the fifth and sixth electron being removed. This is because the sixth electron being removed comes from the 3s sub-shell, which is slightly closer to the nucleus.
- 4) The drastic increase in ionisation energy between the seventh and eighth electrons suggests that the eighth electron comes from a principal quantum shell closer to the nucleus.