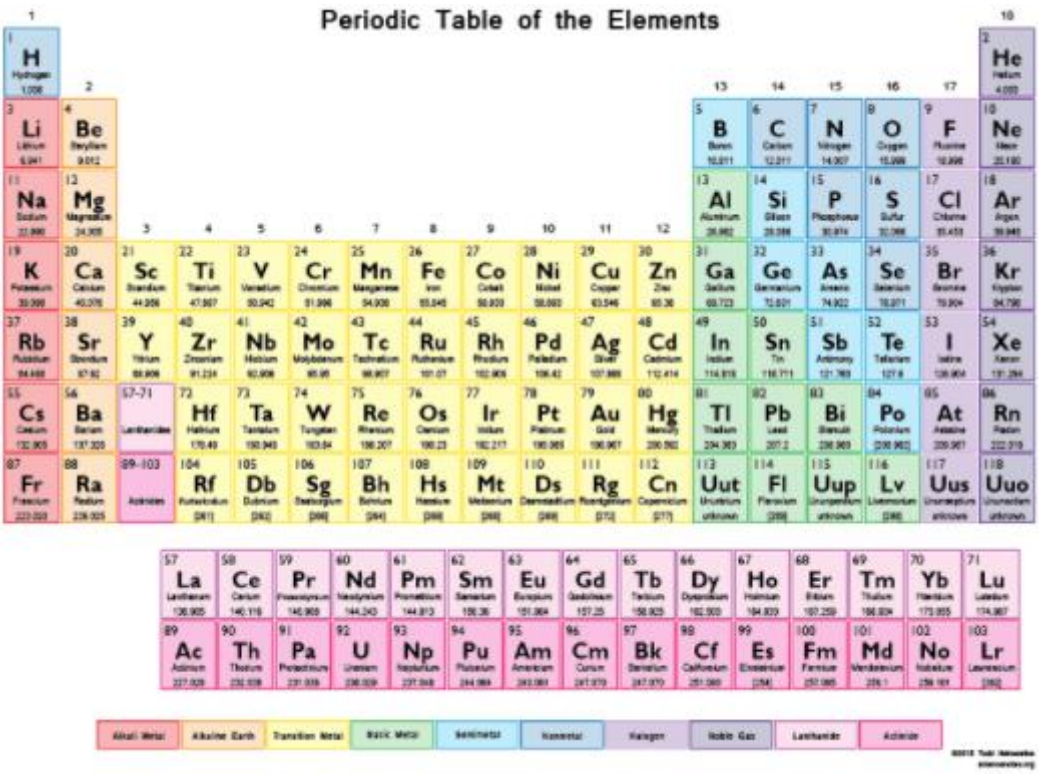
UNIT 1

ATOMIC STRUCTURE AND THE PERIODIC TABLE

PART 2 – INTRODUCTION TO THE PERIODIC TABLE



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Key words: group, period, block, Periodic Law, ionisation energy, electron affinity, atomic size, ionic size

Units which must be completed before this unit can be attempted:
none

1. The Structure of the Periodic Table

The periodic table is a list of all known atoms (and hence elements) arranged in order of increasing atomic number, from 1 to 106. In addition to this, the atoms 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 by arranging the atoms in rows and columns as follows:

- Atoms with one shell are placed in the first row (ie H and He), Atoms with two shells are placed in the second row (Li to Ne) and so on. A row of atoms thus arranged is called a **period**.

- In addition, the atoms are aligned vertically (in columns) with other elements in different rows, if they share a similar outer-shell electronic configuration. For example, elements with outer-shell configuration ns^1 are all placed in the same column (Li, Na, K, Rb, Cs, Fr). A column of atoms thus arranged is called a **group**.

According to these principles, the periodic table can be constructed as follows:

I	II												III	IV	V	VI	VII	0
			H															He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th - Lw															

Since the electronic configurations of H and He are unusual, they do not fit comfortably into any group. They are thus allocated a group based on similarities in physical and chemical properties with other members of the group. He is placed in group 0 on this basis, but hydrogen does not behave like any other element and so is placed in a group of its own.

The elements Ce - Lu and Th - Lw belong in the periodic table as shown above. However if they are placed there periods 6 and 7 do not fit onto a page of A4, so they are placed below the other elements in most tables.

The Periodic Table can also be separated into four distinct blocks, based on the outer shell electronic configuration of the atoms:

The s-block atoms are all those with only s electrons in the outer shell.

The p-block atoms are all those with at least one p-electron in the outer shell.

The d-block atoms 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.

The f-block atoms 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.

I	II												III	IV	V	VI	VII	0
			H															He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th – Lw															

Elements coloured green are in the s-block
Elements coloured blue are in the p-block
Elements coloured red are in the d-block
Elements coloured black are in the f-block

2) History of the Periodic Table

The first scientist to publish a Periodic Table was Dimitri Mendeleev, in 1869.

Previous scientists had discovered and named different elements, and some scientists had also already observed that as atomic mass increases, the properties of the elements vary periodically.

But Mendeleev was the first to attempt to classify every element within a specific row or column in a table:

Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Mendeleev arranged all of the known elements in order of increasing atomic mass, and placed all elements with similar properties in the same column.

Mendeleev used his Periodic Table to predict the discovery of at least six new elements, and to predict the properties of a number of new elements before they were discovered.

By creating the first Periodic Table, Mendeleev became the first scientist to develop a system of **classification** for elements.

3) Trends in the Periodic Table

The physical and chemical properties of atoms (and elements) in the Periodic Table show clear patterns related to the position of each element in the Periodic Table. Elements in the same group show similar properties, and properties change gradually on crossing a period.

The **Periodic Law** states that **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 in known as **Periodicity**.

(a) First Ionisation Energy

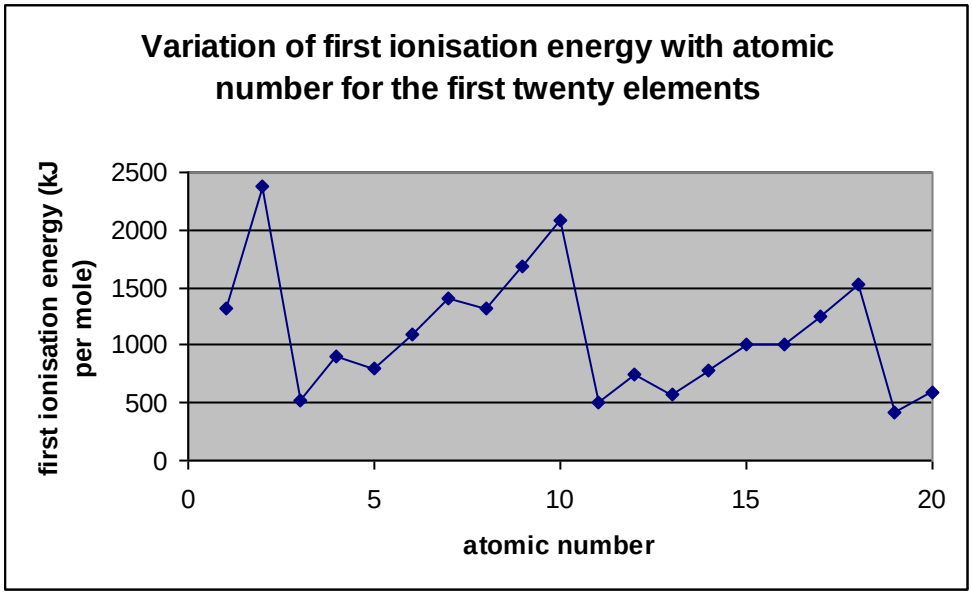
The first ionisation energy of an element is the energy required to remove one electron from each of a mole of free gaseous atoms of that element.

It can also be described as the energy change per mole for the process:

$$\mathbf{M(g) \rightarrow M^{+}(g) + e}$$

The amount of energy required to remove an electron from an atom depends on the number of protons in the nucleus of the atom and on the electronic configuration of that atom.

The first ionisation energies of the first 20 elements in the periodic table is shown below:



There are various trends in this graph which can be explained by reference to the proton number and electronic configuration of the various elements. A number of factors must be considered:

- Energy is required to remove electrons from atoms in order to overcome their attraction to the nucleus. The greater the number of protons, the greater the attraction of the electrons to the nucleus and the harder it is to remove the electrons. The number of protons in the nucleus is known as the **nuclear charge**.
- The effect of this nuclear charge, however, is cancelled out to some extent by the other electrons in the atom. Each inner shell and inner sub-level electron effectively cancels out one unit of charge from the nucleus. This is known as **shielding**.
- The outermost electrons in the atom thus only feel the residual positive charge after all inner shell and inner sub-shell electrons have cancelled out much of the nuclear charge. This residual positive charge is known as the **nuclear attraction**.
- Electrons repel each other, particularly when they are in the same orbital. The degree of **repulsion** between the outermost electrons affects the ease with which electrons can be moved.

The trends in first ionisation energies amongst elements in the periodic table can be explained on the basis of variations in one of the four above factors.

(i) General trend across a Period

Compare the first ionisation energies of H and He. Neither have inner shells, so there is no shielding. He has two protons in the nucleus; H only has one. Therefore the helium electrons are more strongly attracted to the nucleus and hence more difficult to remove. The first ionisation energy of He is thus higher than that of H.

Compare the first ionisation energies of Li ($1s^2 2s^1$) and Be ($1s^2 2s^2$). Be has one more proton in the nucleus than Li, and no extra inner-shell electrons, so the nuclear attraction in Be is higher and the Be electrons are more strongly attracted to the nucleus. The first ionisation energy of Be is thus higher than that of Li.

In general, the first ionisation energy increases across a period because the nuclear charge increases but the shielding remains the same, so the nuclear attraction increases.

(ii) Anomalies

Compare the first ionisation energies of Be ($1s^2 2s^2$) and B ($1s^2 2s^2 2p^1$). B has one more proton in the nucleus (5) than Be (4) but there are also 2 extra inner sub-shell electrons causing shielding. The extra shielding outweighs the extra nuclear charge and so the nuclear attraction decreases. The first ionisation energy of B is thus lower than that of Be. A similar decrease is seen between Mg and Al.

Ionisation energies decrease from group II to group III because in group III the electrons are removed from a p-orbital, so it is shielded by the s-electrons in the outer shell. Thus the nuclear attraction decreases.

Compare the first ionisation energies of N ($1s^2 2s^2 2p^3$) and O ($1s^2 2s^2 2p^4$). Consider the electronic configurations of both atoms:

	1s	2s	2p		
N	↑↓	↑↓	↑	↑	↑
O	↑↓	↑↓	↑↓	↑	↑

Note that in N the electron is removed from an unpaired orbital, but in O it is removed from a paired orbital. In a paired orbital, the two electrons share a confined space and so repel each other. They are therefore less stable and easier to remove. This repulsion effect outweighs the higher nuclear charge in O. The first ionisation energy of O is thus lower than that of N and a similar decrease is seen between P and S.

First ionisation energies decrease from group V to group VI, since the electron removed from the group VI atom is paired, so there is more repulsion between the electrons and the electron is easier to remove.

The trend in first ionisation energies across a period can thus be summarised as follows:

- There is a general increase across the period as the nuclear charge increases and the shielding remains the same, which means that the attraction between the nucleus and the outer electrons increases.

- There is a drop from the Group II atom (eg Be or Mg) to the Group III atom (eg B or Al) because in the Group 3 atom a p electron is being removed and the extra shielding from the s subshell actually causes a fall in the nuclear attraction.

- There is also a drop from the Group V atom (eg N or P) to the Group VI atoms (eg O or S) because the electron in the Group 6 atom is being removed from a paired orbital. The repulsion of the electrons in this orbital makes them less stable and easier to remove.

(iii) Trend down a group

The above graph also shows a clear decrease in first ionisation energy on descending a group. This can be explained in the following way:

On descending a group, the nuclear charge increases but the number of shells also increases, so the shielding increases. The increase in shielding outweighs the increase in nuclear charge, and so the attraction between the nucleus and the outermost electrons decreases. Therefore there is a decrease in first ionisation energy down a group.

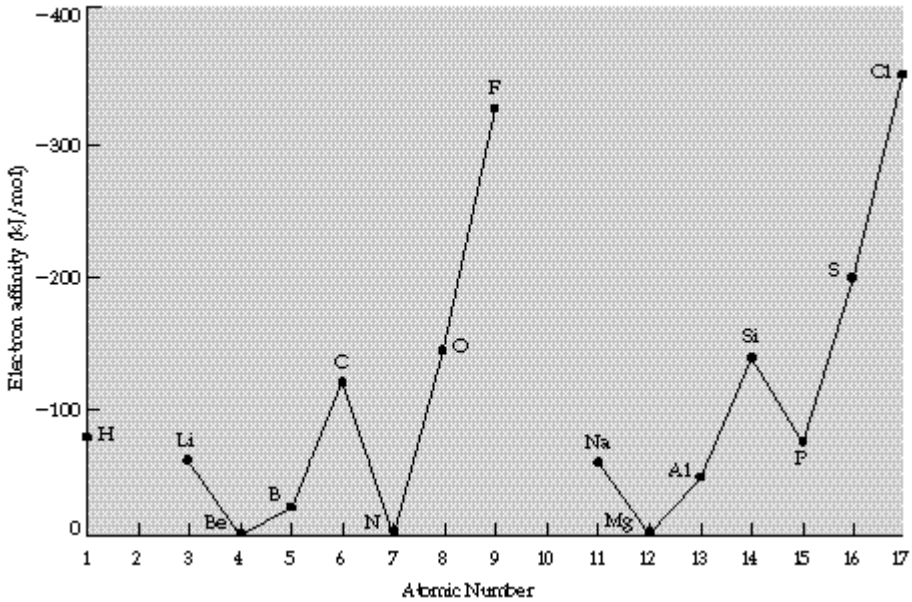
(b) First Electron Affinity

The first ionisation energy of an element is the energy change when one electron is added to each of a mole of free gaseous atoms of that element.

It can also be described as the energy change per mole for the process:

$$M(g)\ e \rightarrow M^{-}(g)$$

The first electron affinities of the first 18 elements in the periodic table is shown below:



The factors affecting the trends in first electron affinity across a Period and down a Group (nuclear charge, shielding and repulsion) are the same as those affecting first ionisation energy, so the Periodic and group trends are very similar:

In general, the first electron affinity increases across a period because the nuclear charge increases but the shielding remains the same, so the nuclear attraction increases.

The first electron affinity decreases from group I to group II because in group II the electron is added to a p-orbital, so it is shielded by the s-electrons in the outer shell. Thus the nuclear attraction decreases.

The first electron affinity decreases from group IV to group V, since the any electron added to the group V atom will be paired, so there is more repulsion between the electrons and the electron is not as easy to add.

On descending a group, the nuclear charge increases but the number of shells also increases, so the shielding increases. The increase in shielding outweighs the increase in nuclear charge, and so the attraction between the nucleus and the outermost electrons decreases and there is a decrease in first electron affinity on descending a group.

Note that the anomalies in the periodic trend in first affinity occur between Groups 1 and 2 and between Groups 4 and 5 because electrons are being added. The anomalies in the periodic trend in first ionisation energy occur between Groups 2 and 3 and between Groups 5 and 6 because electrons are being removed. Otherwise the trends are the same for both ionisation energy and electron affinity.

(c) Atomic Size

On moving across the Periodic Table from left to right, the nuclear charge increases but the shielding stays the same. The attraction of the outer electrons to the nucleus thus increases and the outer electrons are pulled in closer. The size of the atoms therefore **decreases** on crossing a period – i.e. sodium is the largest atom in Period 3 and argon is the smallest.

On moving down the Periodic Table from top to bottom, the nuclear charge increases but the number of shells also increases, and the increase in shielding outweighs the increase in nuclear charge. The outermost electrons are therefore held less closely to the nucleus and drift further out. The size of the atoms therefore **increases** down a group – i.e. beryllium is the smallest atom in group 2 and radium is the largest.

(d) Ionic Size

When you remove an electron from the outer shell, the repulsion between the remaining electrons decreases, and they are able to move closer to the nucleus. Cations are therefore always smaller than the corresponding atoms of the same element.

When you add an electron to the outer shell, the repulsion between the electrons increases, and they are pushed further away from the nucleus. Anions are therefore always larger than the corresponding atoms of the same element.

(e) Summary of Periodic Trends

I	II												III	IV	V	VI	VII	0
			H															He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th – Lw															

low ionisation energy	→	high ionisation energy
low electron affinity	→	high electron affinity
large atomic and ionic size	→	small atomic and ionic size

Atoms on the left-hand side (and the bottom) of the Periodic Table are larger, are easier to take electrons away from and do not attract other electrons strongly.

Atoms on the right-hand side (and the top) of the Periodic Table are smaller, are harder to take electrons away from and attract other electrons strongly.

Test Your Progress: Topic 1 Part 2 Exercise 1

1. State and explain the trend in first ionisation energy across Period 3
2. State and explain the trend in first electron affinity down Group VII
3. Explain why the first ionisation energy of B is lower than that of Be
4. Explain why the first electron affinity of P is lower than that of Si
5. Explain why atoms in the same period get smaller from left to right in the Periodic Table