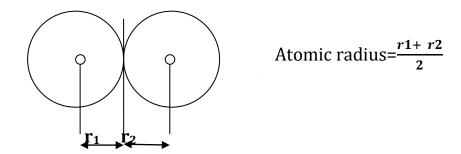
# **Periodic properties**

# Atomic radius (atomic size)

Atomic radius depends on the outermost electrons and determines the size of an atom.

#### **Definition**

Atomic radius is half the distance between the nuclei of two adjacent atoms in the crystal of a noble gas



Therefore, atomic radius is estimated to be half the sum of the distances  $\mathbf{r_1}$  and  $\mathbf{r_2}$  between the nuclei of the two atoms.

Atomic radius is generally the distance of closest approach of one atom to another atom in bonding situation, where at such a distance the inter-nuclear and inter-electronic repulsion just balances with the nuclear-electronic attraction.

Therefore, the electron cloud is not definite, thus the radius of an atom is the distance of closest approach of one atom to another identical atom.

# Factors that determine the size of an atom (atomic radius)

# (i) Nuclear charge

This is force of attraction by the nucleus of an atom for electrons in different energy levels. Its magnitude is determined by the number of protons which exist in the nucleus of an atom or ion of an element.

When the electrons in the different energy levels are strongly attracted to the nucleus, the atomic radius (size) greatly decreases.

## (ii) Screening effect/shielding effect

This is the repulsion that occurs amongst the electrons in the inner energy levels which results into reduction for the nuclear attraction experienced by outermost electrons. The magnitude of screening effect depends on the number of energy levels; the lower the number of energy levels, the lower the screening effect and the higher the number of energy levels, the higher the screening effect.

There are two types of screening effects.

- Primary screening effect
- Secondary screening effect

**Primary screening effect**: This occurs when the repulsion amongst electrons exists between the different energy levels. This is the major form of screening.

**Secondary screening effect**: This occurs when the repulsion is amongst electrons within the same energy level.

Therefore, primary screening effect occurs down the group since electrons are being added in the different energy levels and there is addition of completely filled energy level of electrons from element to another. Secondary screening effect occurs across the period since the electrons are being filled in the same energy level.

**Note**: It is the existence of primary screening effect which results into a decrease in effective nuclear charge and consequently leading to increase in atomic radii. Existence of secondary screening effect causes only very slight increase in screening effect resulting into increase in nuclear charge outweighing the increase in screening effect leading to increase in effective nuclear charge.

# (iii) Effective nuclear charge

This refers to the net force acting on the outer electrons in an atom or ion of an element. Therefore, it is the resultant force that occurs after comparing the trend in variation of both the screening effect and nuclear charge either across the period or down the groups in the Periodic Table.

#### Note:

If the increase in nuclear charge outweighs the increase in screening effect, then there is increase in effective nuclear charge. However, when the increase in screening effect outweighs the increase in nuclear charge, then there is a decrease in effective nuclear charge. Increase in effective nuclear charge results into the outer electrons to become attracted more strongly to the nucleus and vice versa.

#### Variation of atomic radius (atomic size)

## a) Across the periods

#### Period 2

Element	Li	Ве	В	С	N	0	F	Ne
Atomic	0.123	0.089	0.082	0.070	0.068	0.066	0.064	0.060
radius(nm)								

#### Period 3

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic	0.156	0.136	0.125	0.117	0.110	0.104	0.099	0.086
radius(nm)								

#### Trend of atomic radius across the Period

Generally atomic radius decreases from left to right across the period of the Periodic Table.

# **Explanation**

Across the period as you move from one element to the next, a proton is being added to the nucleus of the atoms and this leads to increase in nuclear charge.

At the same time, electrons are being added to the same energy level and therefore increasing the screening effect by electrons only slightly. However, increase in nuclear charge outweighs increase in screening effect of the electrons. This results into an increase in the effective nuclear charge.

Therefore, the outer electrons become strongly attracted closer to the nucleus leading to a decrease in the atomic radius of elements across the period.

#### b) **Down the groups**

Example: Group (I) elements

Element	Atomic radius
	(nm)
Li	1.23
Na	1.57
K	2.03
Rb	2.16
Cs	2.35

#### Trend;

Generally atomic radius increases as you go down the group in the Periodic Table.

## **Explanation**

Down the group from one element to the next, the electrons are being filled in different energy levels and there is addition of a completely filled up energy level with electrons which leads to increase in the screening effect.

At the same time, protons are being added to nucleus of the atoms which results into increase in nuclear charge down the group.

However, the increase in screening effect outweighs the increase in nuclear charge and this results into a decrease in the effective nuclear charge. The outer electrons therefore become less strongly attracted on the nucleus as we move down the group resulting into an increase in the atomic radius.

# **Revision questions**

1. The table below shows the atomic radii of elements of group (II) in the Periodic Table.

Element	Ве	Mg	Са	Sr	Ва
Atomic radius(nm)	0.112	0.160	0.197	0.215	0.221

- (a) (i) State how the atomic radii of the elements vary in the group.
  - (ii) Explain your answer in (a) (i) above.
- (b) Explain how atomic radius affects reactivity of group (II) elements with water.
- 2. (a) Define atomic radius.
  - (b) Explain how the atomic radius varies
    - (i) Across the period;
    - (ii) Down a group in the Periodic Table

# **Ionization energy**

Is the energy required to remove completely one mole of electrons from one mole of gaseous atoms to form one mole of gaseous ions.

#### 0r

Is the energy required to remove an electron from the valence shell of an isolated gaseous atom forming a gaseous ion.

i.e. 
$$M_{(s)} \longrightarrow M^{+}_{(g)} + e$$
 ;  $\Delta H = I.E$ 

#### Note:

Removal of electrons from any atom requires energy and therefore ionization energy is always positive thus an endothermic process. The easier to remove an electron, the lower is the ionization energy. It is easier to remove an electron from a metal atom than a non-metal atom, thus ionization energy for metals is lower than for non-metals. Removing the first loosely held electron requires first ionization energy, removing the next loosely held electron requires second ionization energy etc.

## First ionization energy

This is the amount of energy required to remove one mole of electrons from one mole of gaseous atoms forming one mole of unipositively charged gaseous ions.

i.e. 
$$Mg_{(g)} \longrightarrow Mg_{(g)} + e$$
;  $\Delta H = 1^{st} I.E$ 

#### 0r

Is the amount of energy required to remove an electron from a gaseous atom forming a unipositively charged gaseous ion.

# Second ionization energy

Is the energy required to remove one mole of electrons from one mole of univalently charged gaseous ions to form one mole of divalently charged gaseous ions.

i.e. 
$$Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e$$
;  $\Delta H = 2^{nd} I.E$ 

**3**<sup>rd</sup>, **4**<sup>th</sup> ionization energies e.t.c, is the energy required to remove the third, fourth etc moles of electrons respectively.

 $1^{st}$ ,  $2^{nd}$ ,  $3^{rd}$  e.t.c, ionization energies are collectively referred to as *successive ionization energies*.

**S.I.unit:** Ionization energies are conveniently expressed in kiloJoules per mole (kJmol<sup>-1</sup>) but other units are kilocalories per mole (kcalmol<sup>-1</sup>) and electron volts per atom (eV/atom).

#### Factors affecting the magnitude of ionization energy

#### (i) Atomic radius/ atomic size

The bigger the atomic radius, the lower will be the ionization energy and the smaller the atomic radius the higher will be the ionization energy.

#### **Explanation**

For atoms with small atomic radius, the outermost shell electrons are closer to the nucleus and are strongly attracted to the nucleus hence high energy is required to remove the electrons. For large atomic radius, the outermost shell electrons are far away from the nucleus, thus they are less strongly attracted to the nucleus and easy to remove with low energy hence lowering the value of ionization energy.

**Note:** This also explains the increase in values of successive ionization energies as the atoms/ions become smaller and why on proceeding down the group of the representative elements, ionization energy values generally decrease.

# (ii) Nuclear charge

The greater the nuclear charge provided the screening effect increases only slightly, the higher will be the ionization energy. This is because there will be an increase in effective nuclear attraction for the electrons and therefore increased amount of heat energy will be required to remove the electrons.

The lower the nuclear charge, the lower will be the ionization energy. The outermost shell electrons will be less strongly attracted to the nucleus thus decreased amount of heat energy will be required to remove the electrons.

**Note:** This explains why the ionization energy of lithium ion, Li<sup>+</sup> (3) is higher than that of a helium atom, He. Highly charged nucleus has a greater pull for the electrons.

Both species have the same number of electrons but lithium ion has a greater nuclear charge compared to the helium atom. Therefore, lithium ion exhibits a greater nuclear charge attraction on its outermost electron cloud than the helium atom.

## (iii) Net charge on the ion/atom

The magnitude of successive ionization energies increases generally with increase in the net charge of an ion.

i.e. 
$$1^{st}$$
 I.E <  $2^{nd}$  I.E <  $3^{rd}$  I.E <  $4^{th}$  I.E e.t.c

The bigger the charge on the cation, the higher will be the ionization energy. This is because for every electron removed, there is an extra residual positive charge hence higher effective nuclear charge. The few remaining electrons will experience greater nuclear attraction and as such more heat energy will be required to remove subsequent electrons from the ion thus increase in ionization energy.

#### (iv) The screening effect/ shielding effect

This is the repulsion that occurs between electrons existing in different inner energy levels resulting into reduction for the nuclear attraction experienced by outermost electrons. Increase in screening effect, lowers ionization energy. When the electrons are greatly shielded from the nuclear charge; they will be less strongly attracted towards the nucleus and as such less amount of heat energy will be required to remove the electrons. The lower the screening effect, the higher the ionization energy. This is because the outermost electrons are strongly attracted to the nucleus, thus high amount of heat energy is required to remove outermost shell electrons, increasing the ionization energy.

**Note**: The more, the inner energy levels, the greater the shielding effect thus the lower the ionization energy.

# (v) Electronic configuration of an atom

Completely filled and half filled sub shells are thermodynamically stable and require large amount of heat energy to remove electrons from them. However, those which are completely full are more stable than those which are half filled and therefore require more heat energy to remove electrons from them.

## (vi) **Penetrating power of valence electrons**

This refers to the distance of the electrons within the sub shells from the nuclear charge. An increase in the penetrating power of the valence electrons increases the value of ionization energy. For a given energy level, the penetrating power of the electrons decreases in the order:  $\mathbf{s>p>d>f}$ , where the electrons in the  $\mathbf{s-}$  sub energy level are nearer the nucleus and more penetrating than the  $\mathbf{p}$ ,  $\mathbf{d}$  and  $\mathbf{f}$  electrons. Therefore, the higher the penetrating power, the greater will be the ionization energy. This is because the electrons will be nearer the nucleus and experience greater nuclear attraction thus a lot of heat energy will be required to remove the electrons leading to increase in the ionization energy.

## Revision questions

- (a) Explain the term ionization energy
- (b) Explain how the following factors affect the magnitude of ionization energy.
  - (i) Shielding effect of electrons
  - (ii) Penetrating power of valence electrons
  - (iii) net charge on an atom or ion
  - (iv) atomic size

# Variation of first ionization energy

#### Across the period in the Periodic Table

#### Period 2 elements

Element	Li	Be	В	С	0	F	Ne
1st I.E(kJmol-1)	520	899	801	1403	1310	1681	20180
Atomic number	3	4	5	7	8	9	10

#### Period 3 elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
1st I.E(kJmol-1)	502	745	587	791	1020	1000	1260	1530
Atomic number	11	12	13	14	15	16	17	18

Graphically, the variation is represented by a plot of first ionization energy against atomic number.

#### Assignment

Plot a graph of the first ionization energy against atomic number of the elements for period 2 and period 3 elements.

# Trend;

Generally the first ionization energy increases from left to right across a period as the atomic number increases.

# **Explanation**

Across the period, the nuclear charge increases due to the increase in the atomic number (number of protons). At the same time, there is increase in the screening effect by the electrons added to the same energy level. The increase in the nuclear charge outweighs the increase in the screening effect by the electrons in the same energy level.

This results into an increase in the effective nuclear charge. This increases the electrostatic force of attraction between the nucleus and the outermost shell electrons.

The outermost shell electrons become strongly attracted and closer to the nucleus and the atom decreases in size resulting into an increase in the amount of the heat energy required to remove an electron, thus increase in the value of ionization energy. However, there are exceptionals to the expected general trend. Considering the second short period, the expected order of increase in ionization energy values would be;

*Li <Be<B<C<N<O<F<Ne* but expected order is *Li <B<Be<C<O<N<F<Ne* 

**Explanation** 

The ionization energy of Beryllium is higher than that of Boron.

This is because beryllium atom has a completely filled 2s-orbital with two (2) electrons i.e.  $1s^2 2s^2$ . This makes it thermodynamically more stable than that of boron:  $1s^2 2s^2 2p^1$ ; where the 2p-orbital is under filled with one (1) electron and thermodynamically unstable.

The stable orbital requires more energy for an electron to be removed compared to one which is unstable, thus higher ionization energy of Beryllium compared to the Boron atom.

Similarly, for nitrogen:  $Is^2 2s^2 2p^3$ ; the first electron is being removed from the 2p-orbital which is half filled with three (3) electrons and thermodynamically more stable than the 2p-orbital of oxygen:  $Is2 2s^2 2p^4$ ; which has four (4) electrons and thermodynamically unstable.

Therefore less heat energy is required to remove an electron from a thermodynamically less stable orbital than a stable one. Thus, the  $1^{st}$  ionization energy of nitrogen being higher than that of oxygen.

For similar reasons, the actual order of the variation of 1<sup>st</sup> ionization energy with atomic number of Period 3 elements is: *Na<Al<Mg<Si<S<P<Cl<Ar.* 

First ionization energy of aluminum is less than that of magnesium.

**Explanation** 

**Mg**:  $Is^2 2s^2 2p^6 3s^2$ 

Al:  $Is^2 2s^2 2p^6 3s^2 3p^1$ 

For magnesium, the electron is being removed from the 3s-orbital which is completely full with two (2) electrons and energetically stable. Therefore a lot of heat energy is required to remove an electron, thus high  $1^{\text{st}}$  ionization energy value.

For aluminum, the electron is being removed from the 3p-orbital with only one (1) electron which is neither completely full nor half filled and therefore energetically not stable. Less amount of heat energy will be required to remove this electron, thus low ionization energy value.

Similarly, the first ionization energy of sulphur is less than that of phosphorus.

## **Explanation**

**P:**  $1s^2 2s^2 2p^6 3s^2 3p^3$ 

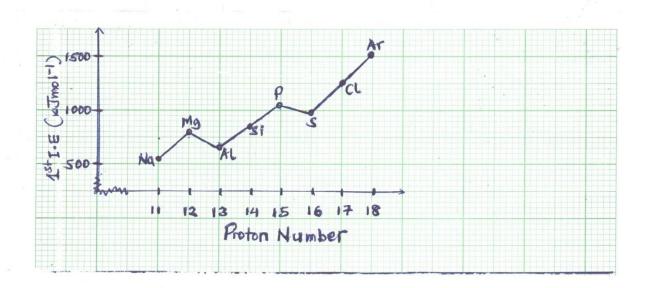
**S:**  $1s^2 2s^2 2p^6 3s^2 3p^4$ 

For phosphorus, the first electron is being removed from the 3p-orbital with three (3) electrons thus half filled and energetically stable. A lot of energy is required to remove an electron.

For sulphur, the electron is being removed from the 3p-orbital with four (4) electrons thus neither half filled nor completely full and energetically unstable. Less heat energy will be required to remove this electron. This makes the first ionization energy of sulphur being less than that of phosphorus.

# Revision questions

- (1) (a) Define the term first ionization energy.
  - (b) The graph below shows the variation of 1<sup>st</sup> ionization energy with atomic number across Period 3 elements in the Periodic Table.



# Explain why the;

- (i) first ionization energy increases overall, across the periods.
- (ii) first ionization energy of magnesium is higher than that of aluminum.
- (iii) first ionization energy of phosphorus is higher than that of sulphur.
- (iv) first ionization energy of magnesium is very high.
- (2) (a) State and explain the trend of the variation of 1<sup>st</sup> ionization energy across period 2 elements in the Periodic Table
  - (b) Briefly explain why the;
    - (i) first ionization energy of beryllium is higher than that of Boron.
    - (ii) first ionization energy of oxygen is less than that of Nitrogen.
- (3) (a) Explain the term ionization energy.
  - (b) Explain how the following factors affect the magnitude of ionization energy.
    - (i) Shielding effect of electrons
    - (ii) Penetrating power of valence electrons
    - (iii) Net charge on an atom or ion

(c) The table below shows the 1<sup>st</sup> ionization energy and atomic numbers in the third period of the periodic table.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
1st I.E(kJmol-1)	502	745	<i>587</i>	791	1020	1000	1260	1530
Atomic number	11	12	13	14	15	16	17	18

- (i) Plot a graph of the 1<sup>st</sup> I.E against atomic numbers of the elements of the third period.
- (ii) Explain the shape of the graph.

# Variation of the first ionization energy down the group in the Periodic Table

Example: Group (II) elements

Element	Atomic number	1 <sup>st</sup> I.E(kJmol <sup>-1</sup> )
Be	4	899
Mg	12	737
Са	20	590
Sr	38	549
Ва	56	503

#### Trend;

The first ionization energy decreases down the group in the Periodic Table.

# **Explanation**;

On descending the group, there is increase in the nuclear charge due to the increase in the number of protons (atomic number). At the same time, there is increase in the screening effect by both electrons and the extra electronic completely filled shells (energy levels). The increase in the screening effect outweighs the increase in the nuclear charge leading to a decrease in the effective nuclear charge. This results into the electrostatic force of attraction of outermost electrons by the nucleus to decrease which leads to a decrease in the amount of heat energy required to remove an electron, thus decrease in the first ionization energy.

# **Successive ionization energies**

These are the energies required to remove successive electrons from gaseous cations to form cations with higher numbers of positive charge i.e.

$$X_{(g)}$$
  $\longrightarrow$   $X^{+}_{(g)}$  + e ; 1<sup>st</sup> I.E  $X^{+}_{(g)}$   $\longrightarrow$   $X^{2+}_{(g)}$  + e ; 2<sup>nd</sup> I.E successive I.Es  $X^{2+}_{(g)}$   $\longrightarrow$   $X^{2+}_{(g)}$  + e ; 3<sup>rd</sup> I.E

The magnitude of successive ionization energies occurs in the increasing order i.e.  $1^{st}$  I.E <  $2^{nd}$  I.E <  $4^{th}$  I.E e.t.c.

## **Explanation**

- (i) The magnitude of ionization energy increases with decrease in the size of the atom or ion from which the electron is being removed. The smaller the ion or atom, the greater the ionization energy since the electrons remaining experience a greater nuclear charge attraction.
- (ii) The magnitude of the effective nuclear charge increases as an electron is removed from the gaseous atom or cation. The proton-electron ratio; increases as the electrons are removed. The remaining electrons experience greater nuclear attraction and decreased screening effect. Thus, more energy is required to remove the subsequent electrons so as to overcome the attraction which results into increase in the successive ionization energies.

# Importance of ionization energy in the determination of the chemistry of an element

Ionization energy provides a basis for understanding the chemistry of an element.

# (a) Atomic number

The number of successive ionization energies indicates the number of electrons present in an atom.

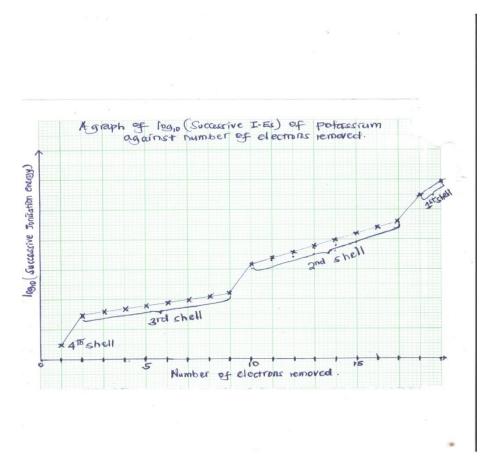
# **Example**

Sodium, Na; has 11 successive ionization energies indicating that the atomic number of sodium atom is 11.

# (b) Arrangement of electrons and distribution in the energy levels

# **Example**

A plot of successive ionization energies of potassium shows distinct breaks.



The potassium atom has four energy levels and therefore belongs to period 4. In the four energy levels, electrons are arranged as:

Shell	n=1	n=2	n=3	n=4
Number of	2	8	8	1
electrons				

Ionization energy also provides information about the presence of sub energy levels. A careful plot of successive ionization energies in the second energy level of potassium atom shows that there are two electrons with almost similar ionization energy which are nearer to the nucleus and followed by six(6) electrons with less energy but almost similar. This shows that the electrons in the second energy level are arranged as follows;

Sub-energy level	S	р
Number of electrons	2	6

#### Note:

The 2s-orbital electrons are more difficult to remove, thus high ionization energy.

From the graph, one can predict;

- Atomic number of an element by counting the number of electrons removed.
- The number of quantum shells/energy levels.
- The period to which an element belongs.
- A group to which an element belongs.

# (c) Determination of metallic and non-metallic character of an element

The magnitude of ionization energy is used as a measure of metallic character of that element.

The first ionization energies of metals are all nearly below 800kJmol<sup>-1</sup> while those of non-metals are all nearly above 800kJmol<sup>-1</sup>.

Down the group, ionization energy decreases and also the elements become more electropositive (more metallic).

Across the period, 1<sup>st</sup> ionization energy increases, so elements become less electropositive(less metallic) but more electronegative (more non- metallic).

#### **Example**

The first three ionization energies of element A, B, C and D are given below.

Element		I.E (kJmol <sup>-1</sup> )								
	1st 1.E 2nd I.E 3rd I.E									
A	740	1500	7730							
В	500	4500	6900							
С	580	1813	9620							
D	1310	3460	5300							

- (a) From the 1<sup>st</sup> ionization energies of the elements, it can be deduced that **B** and **C** have typical metallic properties since their 1<sup>st</sup> ionization energies are well below 800kJmol<sup>-1</sup>.
- (b) Element **A** with its 1<sup>st</sup> ionization energy near 800kJmol<sup>-1</sup> will show some metallic properties.
- (c) From 2<sup>nd</sup> to 3<sup>rd</sup> ionization energy of element A, there is a sudden increase or sharp increase in ionization energy (about five times). This means that, the third electron of element A is removed from a different energy level, thus element A has two electrons in its outermost energy level and therefore is a group (II) element with a positive charge of 2+.

For element **B**, there is an increase in ionization energy of about 9 times from  $1^{st}$  to  $2^{nd}$  ionization energy and an increase of  $1^1/2$  times from  $2^{nd}$  to  $3^{rd}$  ionization energy; therefore element **B** has 1 electron in its outermost shell thus is a group(I) element with a unit positive charge(+).

For element C, from  $1^{st}$  to  $3^{rd}$  ionization energy, the increase is about  $3^{rd}$  to  $3^{rd}$  ionization energy, the increase is about  $2^1/2$  times.

This implies that the 3 electrons are from the same energy level and therefore, element **C** will have a positive charge of 3+, thus belongs to group (III).

For element **D**, its 1<sup>st</sup> ionization energy is above 800kJmol<sup>-1</sup>, thus a non metal.

The following compounds therefore can be formed;

(i) A and D:  $A_xD_2$ 

(ii) B and D:  $\mathbf{B}_{\mathbf{x}}\mathbf{D}$ 

(iii) C and D:  $C_xD_3$ 

# **Revision questions**

1. The first ionization energies of an element B are shown below;

# *Ionization energies (kJmol-1)*

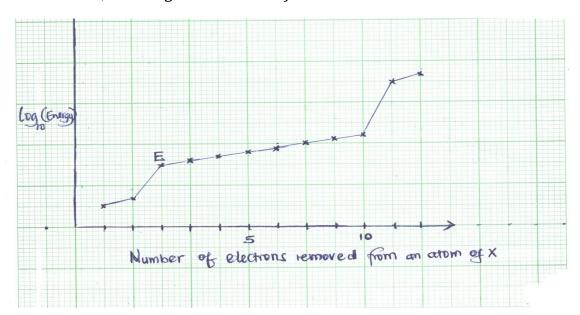
1st	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	6 <sup>th</sup>	7 <sup>th</sup>	8 <sup>th</sup>
<i>786</i>	1580	3230	4360	16000	20000	23600	29100

- (a) Explain what is meant by the term first ionization energy.
- (b) State the factors that determine the value of the first ionization energy.
- (c) To which group in the Periodic Table does the element **B** belong?
- 2. The first four ionization energies of some elements in the same short period of the Periodic Table are shown in the table below:

Element	Ionization energies (kJmol <sup>-1</sup> )							
	1st I.E 2nd I.E 3rd I.E 4th I.E							
W	577	1816	2745	11575				
X	738	1450	7730	10550				
Y	495	4563	691 <i>2</i>	9540				
Z	1255	2297	3849	5163				

- (a) What is meant by the term ionization energy?
- (b) State and explain the trend of ionization energies of the elements.
- (c) (i) State the element that is most likely to form an ion with unit positive charge. Give a reason to your answer.
  - (ii) Write the formula of the chloride of **W**.
  - (iii) Write equation to show how the third electron is removed from **Z**.

3. The diagram below shows the successive ionization energies for an element X, showing the removal of all electrons.



- (a) Giving reasons state;
- (i) the group of elements X
- (ii) the period of element X
- (iii) Identify of element
- (b) Explain the sudden increase in the energy required to remove electron, E.
- (c) Explain how the size of X will change as electrons are removed.
- (d) (i) Explain what would be the sign of the energy change if an electron was added to X to give X-.
  - (ii) How would you expect it to affect the size of X.?
- (e) Explain giving reasons whether you predict X to form compounds in the +1 oxidation state.
- 4. The first ionization energies for elements **A**, **B**, **C** and **D** are given in the table below:

Element	Ionization energies (kJmol <sup>-1</sup> )						
	1 <sup>st</sup>	1 <sup>st</sup> 2 <sup>nd</sup> 3 <sup>rd</sup>					
A	780	1500	7730				
В	500	4560	6900				
С	<i>580</i>	1815	4620				
D	1310	3460	5300				

- (a) Which of the following above are metals?
- (b) To which group in the Periodic Table does element A belong?
- (c) Write the formula of the compound formed between the following:
  - (i) A and D
  - (ii) B and D
  - (iii) C and D

# **Electron affinity**

This is the energy change that occurs when one mole of gaseous atoms gains one mole of electrons to form one mole of negatively charged gaseous ions.

i.e. 
$$X_{(g)} + e \longrightarrow X_{(g)}$$

When gaseous atoms gain electrons, they strongly attract the electrons resulting into release of energy i.e. the process is exothermic

Processes in which elements attain stable electronic configuration after gaining electrons are highly exothermic.

# First electron affinity:

Is the energy change that occurs when one mole of electrons is added to one mole of neutral gaseous atoms to form one mole of uninegatively charged gaseous ions.

i.e. 
$$X_{(g)} + e \longrightarrow X_{(g)}; \Delta H = -XkJmol^{-1}$$

**Note**: The gaining of an electron by an atom is normally an exothermic process.

Example: 
$$O_{(g)} + e \rightarrow O_{(g)}$$
;  $\Delta H = -XkJmol^{-1} (142kJmol^{-1})$ 

The first electron affinity of oxygen is negative. This because during the first electron affinity, the gaseous oxygen atom strongly attracts the electron resulting into energy being released.

However, the second electron affinity is positive (endothermic process)

i.e. 
$$O_{(g)}^{-} + e \longrightarrow O_{(g)}^{2-}; \quad \Delta H = +XkJmol^{-1}(+791kJmol^{-1})$$

This is because the first added electron in the outermost shell repels the incoming electron. Therefore, energy is supplied in order to overcome the repulsive force.

However, the energy supplied is greater than the energy given out after gaining the second electron making the heat change for the second electron affinity process having a positive sign hence being endothermic.

#### Note:

- The magnitude of the first electron affinity is greater than that of second electron affinity making the overall energy change for the process being negative.
- The more negative the electron affinity, the more stable is the anion formed.

## **Examples**

$$F_{(g)}$$
 + e  $\longrightarrow$   $F_{(g)}$   $\Delta H = -328 k J mol^{-1}$   $Cl_{(g)}$  + e  $\longrightarrow$   $Cl_{(g)}$   $\Delta H = -364 k J mol^{-1}$   $I_{(g)}$  + e  $\longrightarrow$   $I_{(g)}$   $\Delta H = -295 k J mol^{-1}$ 

The chloride ion is the most stable while iodide ion is least stable among the halides.

- The abnormally, low value of first electron affinity of fluorine atom is due to the small atomic size. The incoming electron experiences comparatively strong repulsive forces from the electrons around the nucleus in the fluorine atom. This reduces the overall amount of energy released thus low value of the first electron affinity.
- Formation of a divalent ion is endothermic thus a univalent ion is more stable than a divalent ion.

#### **Factors affecting electron affinity**

#### Atomic size

The smaller the size of an atom, the greater is the electron affinity and the larger the size of an atom, the lower the electron affinity.

For small atoms, the incoming electron to be added becomes closer to the nucleus and experiences a greater nuclear force of attraction thus more energy given out leading to increase in electron affinity compared to large atoms where the incoming electron is less strongly attracted towards the nucleus thus decrease in the electron affinity.

#### Effective nuclear charge

Increase in the magnitude of the effective nuclear charge increases the strength of attraction for the electrons to be added. This results into more energy to be released thus increasing the electron affinity.

#### **Screening effect**

The higher the screening effect the lower will be the electron affinity. This is because the electron will be highly shielded from the nucleus and therefore less strongly attracted and as such less amount of heat energy will be released resulting into low electron affinity value.

# **Electronic configuration**

Atoms of elements with either half full or completely full sub energy levels (orbitals) are energetically stable and therefore do not easily gain electrons. As such heat energy must be supplied so as to destabilize the atoms in order for the electrons to be added.

This reduces the magnitude of electron affinity making the value obtained to be less than that expected.

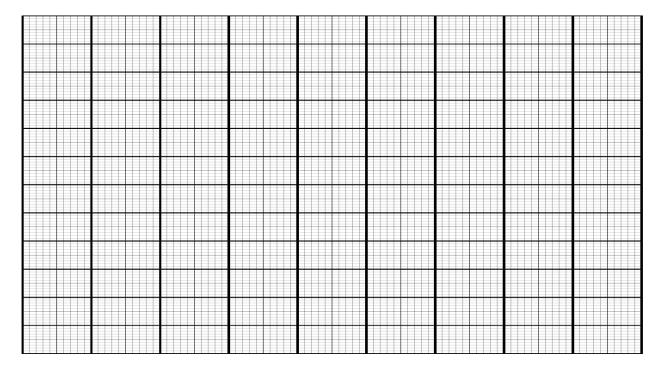
For the atoms of elements whose sub energy levels attain stable electronic configuration when they gain electrons, release a lot of energy resulting into high electron affinity.

#### Variation of first electron affinity across a period

The first electron affinities of the elements in period 3 are given below:

Element	Na	Mg	Al	Si	P	S	Cl
First electron affinity(kJmol-1)	-20	+67	-30	-135	-60	-200	-364
Atomic number	11	12	13	14	15	16	17

Plot a graph of first electron affinity against atomic number



#### General trend:

Generally, there is an increase in electron affinity from sodium to chlorine.

# **Explanation**

The nuclear charge increases because of addition of a proton to the nucleus. The screening effect almost remains the same since an electron is added to the same existing energy level as one moves from sodium to chlorine.

There is therefore a decrease in atomic size from sodium to chlorine due to an increase in effective nuclear attraction for the electrons. As such the electronegativity also increases and therefore the incoming electron become

attracted more strongly as one moves from sodium to chlorine accompanied by sufficient release of heat energy thus general increase in electron affinity.

However, the electron affinity of magnesium is more positive than expected.

This is because the first electron is being added to 3s sub energy level which is completely full with two electrons and energetically stable; Is<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup>. It resists the addition of an electron and as such energy must be supplied to destabilize the magnesium atom before an electron can be added. However, the energy supplied is greater than the energy given out after addition of an electron. This results into the overall energy charge being positive.

Similarly, the first electron affinity of phosphorus is less negative than that of silicon.

P (15): 
$$Is^2 2s^2 2p^6 3s^2 3p^3$$

Si (14): 
$$Is^2 2s^2 2p^6 3s^2 3p^2$$

Phosphorus has a 3p sub energy level which is half full with three electrons and therefore energetically stable and thus resists addition of an electron. Energy has to be supplied in order to destabilize the phosphorus atom before an electron is added. As such less amount of heat energy is given out thus electron affinity being less negative.

For silicon, when an electron is added, it attains a stable electronic configuration with 3p sub energy level being half full with three electrons. This results into much energy being released.

# Variation of first electron affinity down the group

Element	First electron affinity(kJmol-1)
F	-328
Cl	-364
Br	-324
I	-295

#### Trend:

The first electron affinity decreases down the group from chlorine to bromine however, fluorine shows abnormally low value of first electron affinity.

## **Explanation:**

Both nuclear charge and screening effect increase down the group because of addition of a proton to the nucleus and a full shell of electrons respectively.

The increase in screening effect outweighs increase in nuclear charge and thus increase in the atomic size.

As such the electronegativity of the atoms decreases down the group and therefore the incoming electron becomes less strongly attracted towards the nucleus hence less energy being released leading to a decrease in electron affinity down the group.

However, the electron affinity of fluorine is abnormally low due to its small atomic size. The incoming electron experiences strong repulsive forces from the electrons around the nucleus in the fluorine atom. This reduces the amount of heat energy released thus low first electron affinity value for fluorine.

# Revision questions

- 1. (a) Explain how the following factors influence the magnitude of electron affinity.
  - (i) Atomic radii
  - (ii) Electron configuration of element
  - (b) The first electron affinities of the element in period 3 are given in the table below:

Element	Na	Mg	Al	Si	P	S	Cl
$1^{st} E_A$ (kJmol <sup>-1</sup> )	-2.0	+6.7	-3.0	-13.5	-6.0	-20.0	-36.4
Atomic number	11	12	13	14	15	16	17

- (i) Plot a graph of first electron affinity against atomic numbers.
- (ii) Explain the shape of the graph in b (i) above.

2. The first ionization energies and affinities are given in the table below:

Element	1 <sup>st</sup> I.E(kJmol <sup>-1</sup> )	$1^{st} E_A(kJmol^{-1})$
F	1681	-328
Cl	1250	-349
Br	1139	-325
I	1007	-295

- (a) State how the first electron affinities of the element generally vary with their 1st I.Es.
- (b) Explain why the first electron affinity has negative sign.
- (c) Give reason(s) for the abnormally low value of first electron affinity of fluorine.

# **Electronegativity**

This is the measure of the tendency of an atom of an element in a covalently bonded compound to attract electrons towards itself to acquire partial negative charge.

#### 0r

Is the relative ability of an atom of an element to attract bonding electrons towards itself in a covalently bonded molecule.

Small atoms have greater electronegativity values than bigger atoms.

Two atoms with similar tendency to attract electrons will form pure covalent bond in homonuclear molecules e.g.  $O_2$ ,  $H_2$ ,  $Cl_2$  e.t.c

The bond between two atoms with different electronegativities is polarized i.e. partial negative at the end occupied by the more electronegative atom and partial positive at the other end occupied by a less electronegative atom.

# Factors that affect electronegativity

- Effective nuclear charge
- Atomic radius
- Screening effect of the inner electrons

## **Effective Nuclear charge**

The smaller the effective nuclear charge the lower will be the electronegativity.

For a low effective nuclear charge, the bonding electrons experience a low nuclear attraction, the bonding electrons experience a low nuclear attraction leading to a low electronegativity value. The greater the effective nuclear charge, the higher will be the electronegativity.

For a high nuclear charge, bonding electrons experience a higher greater nuclear attraction leading to a high electronegativity value. The greater the effective nuclear charge, the higher will be the electronegativity. For a high nuclear charge, bonding electrons experience a greater nuclear attraction leading to a high electronegativity value.

#### Atomic radius

The smaller the atomic radii, the higher will be the electronegativity.

For a smaller atomic radius the bonding electrons experience a greater nuclear attraction because they are nearer to the nucleus leading a high electronegativity value.

The larger the atomic radii, the smaller will be the electronegativity.

For a large atomic radius, the bonding electrons are far away from the nucleus and experienced a low nuclear attraction leading to a low electronegativity value.

# **Screening effect**

The lower the screening effect, the higher the electronegativity. For a low screening effect, the bonding electrons experience a high nuclear attraction leading to a higher electronegativity value.

The greater the screening effect, the lower the electronegativity. For a high screening effect, the bonding electrons experience a low nuclear attraction leading to a low electronegativity value.

# Variation of electronegativity across a Period

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.3	3.0

**Trend**: *Electronegativity increases from sodium to chlorine (across the Period).* 

# **Explanation**

In moving from left to right across the Period, the nuclear charge increases while the screening effect remains more or less the same. Therefore, the effective nuclear charge increases leading to increased nuclear attraction for the bonding electrons and hence increase in electronegativity.

## Variation of electronegativity down a group

Example: Group (VII) elements

Element	Electronegativity value
F	4.0
Cl	3.0
Br	2.8
I	2.5

**Trend:** Electronegativity decreases from fluorine, chlorine, bromine to iodine (down the group)

# **Explanation**

Down the group, both nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge because an extra shell added as one moves from one element to the next. Therefore, the effective nuclear charge decreases leading to a decrease in nuclear attraction for the bonding electrons and hence decrease in electronegativity.

## **Revision questions**

- 1. (a) Explain what is meant by electronegativity.
  - (b) Explain how the following factors affect the value of electro negativity of an element.
    - (i) Atomic radius
    - (ii) Nuclear charge
    - (iii) Screening effect of the inner electrons.
  - (c) Explain the difference between electronegativity and electron affinity.
- 2. Explain the following;
  - (a) Chlorine is more electronegative than bromine.
  - (b) Fluorine is more electronegative than chlorine.

# **Electropositivity**

Is the ease by which an atom losses one or more electrons to become a positively charged ion.

#### $\mathbf{0r}$

Electro positivity of an element is the tendency of an atom of an element to lose one or more electrons forming gaseous cations or positively charged ions.

The measure of the tendency of an atom of an element to lose electrons is the ionization energy.

Elements with low ionization energy values are highly electropositive while those with high ionization energy values are highly electronegative.

Electropositive elements are those which lose one or more electrons easily to form positively charged ions. Metals are highly electropositive.

## Variation of electropositivity across a Period

**Trend:** *Electropositivity decreases across a period in the Periodic Table.* 

## **Explanation:**

Across the period, the effective nuclear charge increases due to increase in nuclear charge and a more or less constant screening effect.

The electrons present in the atoms become more strongly attracted to the nucleus as one moves across the period. The electrons therefore become more difficult to remove a cross a period leading to decrease in electropositity.

## Variation of electropositive down a group

**Trend**: Electropositivity increases down a group in the Periodic Table.

## **Explanation:**

Down the group, there is increase in nuclear charge and the screening effect but the increase in shielding effect outweighs that due to nuclear charge because of an extra shell of electrons added as one moves from one element to the next.

The effective nuclear charge therefore decreases leading to a decrease in nuclear attraction for the outermost electrons and hence they are easily lost i.e. electropositivity increases.

# Factors affecting electropositivity

# Effective nuclear charge

Increase in effective nuclear charge increases nuclear attraction for the outermost electrons hence they are less easily removed.

# **Screening effect**

Electropositivity increases with increase in screening effect because increase in screening effect reduces nuclear attraction for outermost electrons hence electrons are more easily lost.

#### **Atomic radius (atomic size)**

Electropositivity increases with increase in atomic radius (atomic size). This is because, the larger the atom, the lower the effective nuclear attraction for the outermost electrons and hence the easier the loss of electrons.

#### **Electronic configuration**

Electropositivity is low when the outermost sub shell is either half filled or fully filled because of the high stability and hence more difficult to remove an electron.

# **Boiling and melting points**

#### **Boiling point:**

Is the constant temperature at which a pure liquid changes into vapour at standard pressure (760mmHg).

## **Melting point:**

Is the constant temperature at which a pure solid changes in to liquid at standard pressure. At the melting point, the pure solid is in equilibrium with its pure liquid.

# Factors which affect the magnitude of boiling and melting points of metals

(i) Number of electrons used per atom during metallic bond formation.

	Soft		Hard
Element	Na	Mg	Al
Number of electrons per atom	1	2	3
Melting point	lowest		highest

The strength of metallic bonding increases with increase in the number of electrons contributed per atom to the charge cloud during formation of metallic bond.

Sodium contributes one electron per atom to the charge cloud therefore resulting into formation of weak metallic bond responsible for low melting point of sodium and its softness.

Aluminium contributes three electrons per atom to the charge cloud, therefore forms stronger metallic bonds which are responsible for high melting point and hardness.

#### (ii) Atomic radius

For atoms with small atomic radii, their bonding electrons are strongly attracted to the nucleus making the inter-atomic distance shorter. This results into close packing for the individual atoms thus stronger inter-atomic forces of attraction that require a lot of heat to be broken thus high melting points.

Atoms with large atomic radii, their bonding electrons are less strongly attracted to the nucleus making the inter-atomic distance longer. This leads to less packing of individual atoms resulting into less strong inter atomic forces of attraction that require less heat energy to be broken thus low melting points.

## Factors that affect melting point of non-metallic elements

- (i) Molecular mass
- (ii) Number of electrons used for covalent bonding
- (iii) Number of atoms which are covalently bonded together

#### Revision exercise

Explain how the above factors affect the magnitude of melting point of non-metallic elements.