

# CHEMISTRY NOTES

## Instructions.

- **READ AND WRITE THESE NOTES PLEASE**
- **Equations and Diagrams will be elaborated during lessons.**

## PERIODICITY

The periodic table of elements is the chart in which the known chemical elements are listed in order of increasing atomic number with chemically similar elements occupying the same vertical columns.

The periodic table consists of two major divisions

i) periods: this is the horizontal arrangement of elements. There are 7 periods.

ii) groups: this is the vertical arrangement of elements

There are 8 groups. Groups 1 to V11 are sub divided into A and B thus we can talk of I've and IV B.

Group V111 has 3 columns which include the groups containing iron nickel and cobalt respectively The

Noble gases belong to group O

The periodic table is as shown on the next page

Leave one page for the periodic table

It should be noted that there is no special resemblance between the chemistry of the subgroups A and B eg IV A elements are not related to IV B elements except perhaps their valencies

The division into subgroups is merely a method used by Mendeleev in his original periodic table

For simplicity we shall be merely referring to 1, 11, 111 etc

On analysis, it is observed that the elements within the same outer electronic configuration and similar chemical properties. However no element is exactly the same as another

Elements within the same group show;

Similar properties due to their similar outer electronic configuration

A gradual change in properties down the group due to gradual change in electronegativity down the group

However the first member in any group usually shows anomalous behavior due to high electronegativity small size and restriction to an octet of valence electrons.

Elements usually exhibit valency corresponding to their group number eg group 1 A elements have a valency of 1.

In some cases the elements can also exhibit a valency of 8 minus the group number. Eg phosphorus uses a valency of 5 & 3 (8-5), sulphur exhibits a valency of 6 & 2 (8-6) etc

There is also a gradual change of properties across a period

## Parts of the periodic table

The periodic table is divided into blocks of elements according to the type of orbitals (sub energy level) in which the last electrons are filled. Or valence electrons occupy.

### The S-block

The S-block consists of elements having their outer electrons in the S-orbital.

Elements with one S-electron in the outer energy level are called group I elements (the alkali metals)

Elements with 2 S-electrons in their outer most sub energy level are called group II elements (alkaline earth metals)

In other words the two groups constitute the S-block. Their properties are as a result of S-electron eg group I elements include lithium, sodium, potassium, cesium and rubidium.

Group II elements include beryllium, magnesium, calcium, strontium and barium

the P-block

It consists of elements having their outer most electrons in the P-orbital (sub-energy level) Elements

with 3 electrons in their outer energy level are called group III elements.

Elements with 4 electrons in their outer most energy level are called group IV elements

Groups V, VI, VII have 5, 6, 7 electrons respectively in their outer most energy level

Group III to VIII have the P-orbitals being filled and therefore forms the P-block.

### The d-block elements

These are elements in which the d-orbital is being filled ie

these are elements having electrons in the d-orbital

### Periods

A period is the row arrangement of elements in the periodic table starting with alkali metals ending with the Noble gases The period in which an element belongs corresponds with the number of energy levels the element has.

### Transition elements

Transition elements are elements having partially filled d-orbitals eg 3d-orbitals

Examples of transition elements include

Manganese with electronic configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Iron with electronic configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Transition elements are metals and their ions or compounds are generally coloured

They form complexes have catalytic properties have variable oxidation States. Transition series begin from VIII B to I B

VARIATION OF PERIODIC PROPERTIES

## VALENCY

Valency of an element is the number of electrons lost or gained or shared by an atom during bonding with one or more elements.

Valency remains the same down the group but varies from 1-6 across a period

## METALLIC CHARACTER (ELECTROPOSITIVITY)

There is a gradual change to metallic character to nonmetallic character on passing from left to right of the periodic table.

The oxide of sodium and magnesium are basic, aluminum oxide is amphoteric while the oxides of the period three are acidic.

However metallic character increases down the group

## MELTING POINT

Melting point is the constant temperature at which a pure substance turns from solid state to liquid state at a given pressure when the two states are in equilibrium.

### Factors determining the melting point

For metallic structure the melting point depends on the following factors

i) the number of valency electrons each atom contributes towards the metallic ion.

The higher the number of electrons, the stronger the bond and the higher the melting point. ii)

the metallic radius.

The smaller the metallic radius, the shorter metal-metal bond (or element-element Bond) and the stronger the bond and the higher the melting point and vice versa

Therefore melting point reduces with increase in metallic radius iii)

type of crystal structure

For non metals or metallic structure or molecular substances the melting point depends on the following factors i)

the molecular mass or size of molecule

The higher the molecular mass the higher the melting point and vice versa

ii) the shape of molecules iii) surface of the molecules iv) type of the

structure formed

Giant molecular or atomic structure eg in silicon and diamond have very high melting points due to a large number of covalent bonds that have to be broken before melting occurs.

Simple molecular structures eg in iodine chlorine etc have very low melting points since their molecules are held by Vander waals forces.

v) the way molecules are packed in the solid ie type of close packing of molecules in solid

Closely molecules have higher melting points compared to the less closely packed.

vi) the type of inter molecular forces of attraction

Ionic and covalent bonds have high melting points while those molecules having weak Vander waals forces between their molecules have low melting points

### Question

What is meant by the term melting point?

State the factors that affect the melting points of

i)metals ii) molecular substances

(non metals)

### Variation of melting points down the group

#### Eg melting points of the group 1

Element	Li	Na	K	Pb	Cs
Melting point (°C)	180	98	63	39	29

**Trend:** generally the melting points of the elements decrease down thw group

Explanation

Descending down the group, the atomic radius increases thus the element-element bond becomes longer and weaker and such a decrease in melting point Or

As you move down the group, the size of the positive ions increases, decreasing the charge density.

The force of attraction between the bonding electrons and ion decrease hence a decrease in melting point **Question**

Explain the trend of melting of the elements of

i) group 11 elements ii)

group V11 elements

i) the melting points of group 11 elements decrease down the group.

This because down the group, the size of the positive ion increases thus decreasing the change density.

The force of attraction between the bonding electrons and the positive ions decreases. This decreases the melting point

Or alternative like above iii) the melting point of group V11 elements increases down the group

Explanation

The group V11 elements form diatomic molecules that are held by weak Vander waals forces

The strength of those Vander waals forces increase with increase in molecular mass down the group. Therefore the Vander waals forces increase in the melting point

### Variation of melting point of elements accross a period

### Eg period 3

Elements	Na	Mg	Al	Si	P	S	Cl
Atomic number	11	12	13	14	15	16	17
Melting point (°C)	98	650	660	1410	44	120	-101

### Explanation

Trend: there is a general increase in melting point from sodium to silicon and a general decrease from silicon to chlorine or argon.

Explain

Sodium, magnesium and aluminum are held by **strong metallic bonds** thus forming **metallic structures** which require very high energy for the bonds to be broken hence high melting points.

**The strength of the metallic bonds increase from sodium to aluminum because of the increase in number of electrons contributes per atom towards the metallic bond and also due to decrease in metallic radius eg aluminum has a smaller atomic radius than magnesium and sodium and therefore forms slightly stronger metallic bonds which are more difficult to break.**

The melting point of aluminum is therefore slightly higher than that of magnesium which is higher than that of magnesium which is higher than that of sodium

Silicon forms a **given atomic structure** with very many (4) strong **covalent bonds** which have to be broken before melting occurs hence the abnormally high melting point

Phosphorus, sulphur, chlorine, argon, form **simple molecular structures**. Their molecules are held by weak Vander waals forces whose strength increases with increase in molecular mass hence a sharp decrease in melting point from silicon to phosphorus.

The melting point of phosphorus is lower than that of sulphur because sulphur forms S<sub>8</sub> rings, with higher molecular mass than phosphorus which forms P<sub>4</sub> ring.

Chlorine is diatomic and argon monatomic molecular mass decreases in the order of S<sub>8</sub> greater than P<sub>4</sub> greater than Cl<sub>2</sub> greater than argon Are hence melting point in the same order

### Question

#### No 6b) JJEB 2014 P2

The table below shows the melting points of period 2 elements

Melting point°C	Li	Be	B	C	N	O	F	N
Melting point	454	1551	2573	3925	363	54.8	53.5	24.5

i) state the factors that affect the melting point of elements ii) describe how the

factors you have mentioned affect the melting points (7marks) Solution

i) the number of electrons available for bonding

The atomic radius (element-element bond) and therefore it's bond strength The

Crystal structure of the elements

ii) on moving from left to right along period 2 the melting point increases from lithium to carbon and then decreases abruptly for the non metallic elements. This is because the number of electrons available for bonding increase from once for lithium and for carbon.

As atomic radius decreases from lithium to carbon the inter atomic bonds become shorter and stronger.

There is a change in crystal structure of the elements

Lithium has atoms less efficiently packed than beryllium, boron and carbon form giant molecular structures composed of large number of covalently bonded atoms with carbon more strongly bonded than boron.

The non metals nitrogen to flourine form simple molecular structures with the molecules held together by weak intermolecular forces of attraction. Their melting point is therefore low.

Neon is monatomic.

## Question 2

### UNEB 2007 PAPER 2

4a) the melting point and atomic number of magnesium, aluminum, phosphorus and chlorine, members of period 3 of the periodic table are given in the table below

Element	Mg	Al	P	Cl
Melting point (°C)	649	661	44	-101
Atomic number	12	13	15	17

Explain the trend

Solution

Melting point increases from magnesium to aluminum and then decreases from aluminum to chlorine

Magnesium and aluminum are held by strong metallic bonds thus form giant metallic structures with very high melting point.

Aluminum has very small atomic radius than magnesium and contributes more electrons to the metallic bond than magnesium. It therefore forms slightly stronger metallic bonds which are difficult to break. The melting point of aluminum is therefore slightly higher than that of magnesium.

Phosphorus and chlorine forms simple molecular structure. Their molecules are held by weak Vander waals forces whose strength depend on molecular mass.

Phosphorus forms P<sub>4</sub> molecules with large molecular mass than that of chlorine which forms diatomic molecular (Cl<sub>2</sub>)

Phosphorus therefore has stronger Vander waals force between it's molecules than chlorine hence higher melting point.

## BOILING POINT

Boiling point is the constant temperature at which the liquid vapor pressure balances with the external atmospheric pressure

Like melting point, the boiling point depends on the forces binding the molecules. Therefore the boiling point shows similar trend to the melting point accross the period

### Example

The atomic number and the boiling point of elements in period 3 of the periodic table are as shown below

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic number	11	12	13	14	15	16	17	18
Boiling point in K	1250	1400	2750	2900	500	550	400	0

a) plot a graph of boiling point against atomic number ii)

explain the shape of the graph you have drawn in ai)

### Explanation

Sodium, magnesium and aluminum have giant metallic structures with their atoms held by strong metallic bonds. From sodium to aluminum the atomic radius decreases and the number of electrons contributed per atom to the metallic bond increases and the strength of the metallic bond increases

Silicon has a giant atomic or molecular covalent structure with the atoms held together by strong covalent bonds on

Phosphorus, sulphur, chlorine, and argon have simple molecular structures which are covalent. Their molecules are held by weak Vander waals forces whose strength increases with increase in molecular mass.

Phosphorus is tetra atomic with P<sub>4</sub> molecules. sulphur is octa atomic with S<sub>8</sub> molecules, chlorine is diatomic with Cl<sub>2</sub> molecules and argon is monatomic. The molecular mass increases from phosphorus to sulphur and decrease from sulphur to argon hence boiling point increases from phosphorus to sulphur and decreases from sulphur to argon DENSITY

Density is mass per unit volume.

There is an increase in density across period 3 reaching a maximum at group (iv) elements. This is due to increasing atomic mass with reducing atomic radius

## ATOMIC RADIUS AND IONIC RADIUS

Atomic radius is half the inter nuclear distance between two covalently bonded atoms.

## IONIC RADIUS

Ionic radius is half the inter nuclear distance between two neighboring monatomic ions with a crystalline salt.

The ionic radius of anions is always greater than that of a neutral atom.

Explanation

An anion is formed when an element accepts an electronic. The proton to electrons ratio decreases and the remaining electrons are less strongly attracted by the nucleus causing an increase in the radius of the ion.

The ionic radius of a cation is always smaller or less than that of a neutral atom.

Explanation

A cation is formed when an atom loses an electron. The proton electron ratio increases hence the remaining electrons are attracted more strongly by the nucleus causing a decrease in the radius.

Question 8c) uneb 2015 P2 Explain

the observation

Sodium ion is smaller than sodium atom where as a chloride ion is larger than a chlorine atom.

Solution

The sodium ion is formed by loss of an electron. The nuclear attraction for the remaining electrons increases

There is also a reduction in the number of energy levels filled with electrons

The chloride ion is formed by gain of an electron. The nuclear attraction for the greater number of electrons reduces.

Note: **factors affecting atomic or ionic radius**

Atomic radius and ionic radius largely depends on two factors i)

nuclear charge

This is the force of attraction of the electron by the nucleus

If all other factors are constant, atomic radius decreases with increase in nuclear charge

This is because increase in nuclear charge causes an increase in attraction of the outer most electrons by the nucleus this reducing atomic radius or ionic radius

Note

Because of influence from other factors, it is not uncommon to find an atom with high nuclear charge having a larger atomic radius than an atom even though the atomic radius of sodium (atomic number 11) is larger than magnesium (atomic number 12)

Note that a high atomic number and therefore high number of protons implies a high nuclear charge ii) Screening effect or shielding effect



This is the repulsive of the outer most electrons from the nucleus by those in the inner energy levels

Increase in screening effect increases the atomic radius

A very high screening effect on the outer electrons by the inner electrons implies that the less closely are outer most electrons attracted (or the outer most electrons are effectively shielded from the nuclear charge)

Consequently the outer most electrons will receive less nuclear attraction causing an increase in atomic radius.

Or

The smaller the screening effect, the more strongly are the outer most electrons attracted by the nucleus and the smaller the atomic radius.

Note

#### 1. Primary screening effect

This is the reduction in nuclear attraction force of the outer electrons caused by the electrons present in the inner energy level

#### 2. Secondary screening level

This is a slight reduction in nuclear attraction force for the electrons in the same energy level caused by the natural repulsion between electrons in the energy level of the same charge

#### 3. Effective nuclear charge (nuclear attraction)

This is effective nuclear attraction as a result of subtracting screening effect from nuclear charge.

Effective nuclear charge = nuclear charge - screening effect

Charge density =  $\frac{\text{charge}}{\text{atomic radius}}$

### Variation of atomic radius down the group

Eg group 1 elements

Group 1 elements	Atomic radius (Å)
Li	1.23
Na	1.57
K	2.03
Pb	2.16
Cs	2.35

Trend: atomic radius increases down the group

Explanation

Down the group both nuclear charge and screening effect increase but the screening effect increases more than the nuclear charge due to extra full energy level of electrons added down the group. The nuclear attraction for the valence electrons (effective nuclear charge) reduces down the group resulting in the increase of atomic radius or size.

## Variation of atomic radius (size) across the period

Period 3

Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius	0.156	0.136	0.125	0.117	0.110	0.104	0.099

Trend: across the period atomic radius decreases from left to right

Explanation

Across a period both nuclear charge and screening effect increase but the increase in nuclear charge outweighs the increase in screening effect because an electron is added to same main energy level and proton is added to nucleus.

The nuclear attraction (effective nuclear charge) of the valence electrons increases. Electrons are attracted more towards the nucleus leading to a decrease in atomic radius

### Question 6uneb 1996 P2 no 6

- a) what is meant by the term atomic radius?  
b) explain how atomic radius varies  
i) along a short period of the periodic table ii)  
down the group of the periodic table shown

Solution

- b) first state the trend and then explain

Variation of atomic radius among the transition elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125

Trend: there is a general slight decrease in atomic radius as the atomic number increases

Explanation

As atomic number increases, the nuclear charge also increases. However the electrons are being added to the 3-d subenergy level. These electrons are poorly shielded from the nuclear charge. The nuclear attraction for the outer electron therefore increases leading to the decrease in atomic radii

There is a slight increase in atomic radius from nickel to copper because 3d subenergy level in copper is fully filled with electrons. This increases the shielding of the outer electrons from the nuclear charge thus atomic radius increases IONISATION ENERGY (I.E)

When an atom is made to lose an electron, it is said to be ionised. It becomes positively charged and is known as a cation. To remove an electron from an atom requires energy which is called ionisation energy

What is ionisation energy

This is the minimum amount of energy required to remove one mole of gaseous atoms or gaseous cations to form one mole of positively charged gaseous ions.



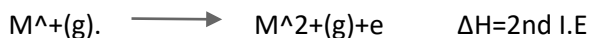
The energy required to remove 1 mole of electrons from a mole of neutral gaseous atom is called first ionisation energy defined as;

The first ionisation energy is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively gaseous cations eg for sodium atom the equation for first ionisation energy is represented as

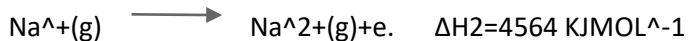


When one mole of electrons is removed from one mole of unipositively charged cation(s) then energy used is second ionisation energy

The second ionisation energy an element is the minimum amount of energy required to remove one mole of electrons from one mole unipositively charged gaseous cation to form one mole of gaseous depositive cation



There can be a third, fourth etc ionisation energy



Ionisation energy is measured in  $\text{kJ MOL}^{-1}$  and is determined from the Spectra.

### Determination of ionisations energy

Ionisation energy can be determined using a value containing gaseous atoms of elements

The filament is heated and gives off electrons

The grid Y is charged positively while the metal plate M is charged negatively.

Current doesn't flow if the potential is zero.

The potential on the grid is increased and the electrons emitted by the filament are now attracted and accelerated by the grid.

In the process of traveling the electrons collide with the gaseous atoms of the element and knock off an electron from the atom and hence causing ionisation.



The electrons are attracted to the grid while the positive ions are attracted to the metal plate M.

Current thus will flow and the minimum grid potential required for ionisation of the atom is measured and is called ionisation potential.

Information about metallic and non metallic character of element.

The first ionisation energies of non metals are all nearby above  $800\text{KJmol}^{-1}$

Down the group the ionisation energies decrease so that the element becomes more metallic.

Eg in group V1 there is exchange from non metallic to metallic character

Across the period first ionisation energy increases. The elements become less metallic.

#### 4. Information about the properties of elements

Ionisation energy is used to predict the properties of elements.

Examples

The first ionisation energies for elements A,B,C,D are given in the table below.

Element	Ionisation energies in $\text{KJmol}^{-1}$		
	1st	2nd	3rd
A	780	1500	7730
B	500	4560	6900
C	580	1815	4620
D	1310	3460	5300

a) From the first ionisation energies of the elements it can be deduced that elements B and C have typical metallic properties since the 1st I.E are well below 800KJmol<sup>-1</sup>

b) element A with first ionisation energy of 780 KJmol<sup>-1</sup> also would show metallic properties

c) i) moving from 2nd to the 3rd I.E for A, there is increase of about 5times.

This means the 3rd electron of A comes from different energy level hence A has 2 electrons in it's outer most energy level. A therefore is in group 11 with charge of +2

ii) for the element B, there is an increase of about 9times from the first to the second ionisation and an increase of about 1.5 times from the 2nd to the 3rd I.E

Therefore element B has one electron in it's outer most shell and thus is a group 1 element and would have a charge of +1

iii) in element C from the first to second I.E there is an increase of about 3 times and from the 2nd to the 3rd by about 2.5 times. Therefore there is a similar rise in ionisation energy on

This implies that the first 3 electrons in C are from the same energy

d) element D with it's ionisation energy well over 800 KJmol<sup>-1</sup> is a non metal.

The following compounds therefore would be formed between i) A and B ii)

B and D iii) C and D

Example

The table below shows the ionisation energies of five elements lettered A,B,C,D,E

Element	First ionisation energy	2nd ionisation energy	3rd ionisation energy	4th ionisation energy
A	500	4600	6900	9500
B	740	1500	7700	10500
C	630	1600	3000	4800
D	900	1800	14800	21000
E	589	1800	2700	11600

a) which one of those elements is most likely to form an ion with a charge of +1. Give a reason for your answer b)

to which group does B belong? Give a reason for your answer

c) state two element which belong to the same group in the periodic table and the groups to which they belong. Solution

a) A:

The second ionisation energy is about 9times the 1st ionisation energy is 1.5 the 2nd I.E and the 4th I.E is 1.5 times the 3rd. This means the A is in group 1 hence from +1

b) B belongs to group 11

This is because of third ionisation energy is about 5 times the 2nd ionisation energy yet 2nd I.E and the 4th I.E is about 1.5 times the third

c) B and D belongs to the same group. Question

The 1st, 2nd, 3rd and 4th ionisation energy of an element Y are 736, 1451, 7740 and 10500 KJ<sup>MOL</sup><sup>-1</sup> respectively.

State the group in the periodic table to which Y belongs and give a reason for your answer

Group II

This is because the largest increase in ionisation energy is from the second to the third ionisation energy.

This shows that there are two electrons in the outer most energy level and the third ionisation energy involves removing an electron from a full new inner energy level.

i) explain the second ionisation energy is greater than the first ionisation energy Solution

First ionisation energy involves removing an electron from a neutral atom whereas the second ionisation energy involves removing an electron from an already positively charged ion.

Although nuclear charge remains same in both cases the nucleus would attract fewer electrons in case of the second ionisation energy.

These fewer electrons will experience greater nuclear attraction resulting in a higher second ionisation energy.

UNEB 2000 P2 NO 2b)

The second and the third ionisation energies of magnesium are 1450 KJ<sup>MOL</sup><sup>-1</sup> and 7730 KJ<sup>MOL</sup><sup>-1</sup> respectively

Give a reason for the large difference between the second and third ionisation energy of magnesium

Solution

Magnesium has the electronic configuration  $1s^2 2s^2 2p^6 3s^2$ . This means that the first two electrons of magnesium are in the outer most energy level.

Removal of the second electron from  $Mg^+(1s^2 2s^2 2p^6 3s^1)$  to form  $Mg^{2+}(1s^2 2s^2 2p^6)$  involves leaving a fully filled 2p orbital which is very stable.

Therefore the second ionisation energy is low compared to the third ionisation which involves removing an electron from a half filled 3s orbital which is less stable than full 3p orbital is low compared to the third ionisation energy which involves removing an electron from a full 2p orbital which is more stable and in another energy level. Therefore the third ionisation energy is high compared to the second

Question 12 p1 1998

The diagram Below shows I.E for an element X showing removal of all electrons

a) giving reason state

i) the group of element X

Group 2

Because X contain two electrons in the outer most shell ii)

the period of electron X

Period 3

The outer most electron in quantum shell is 3

iii) identify element X

Magnesium

b) explain the sudden increase in the energy required to remove electron E

Electrons are being removed from a new energy level

c) explain how the size will change as electrons are removed

The size decreases

Reason

The nuclear charge remains the same.

The remaining electrons are strongly attracted to the nucleus and are drawn closer.

d) explain what would be the sign of energy charge if an electron was added to X to get X Negative ii) how would you expect it to affect the size of X

Size would increase

Attraction by the nucleus on each electron reduced

e) explain giving reason whether you would predict X to form compound in +1 oxidation state

Will not form compounds of oxide state +1.

They would be unstable.

ELECTRON AFFINITY (A.E)

Electron affinity is the reverse of ionisation energy. It is defined as below

Electron affinity is the energy change that occurs when one mole is added to one mole of gaseous atom to form one mole of negatively charged gaseous ion.



Or

Electron affinity is the energy charge that occurs when an electron is added to a gaseous atom to form a gaseous anion

Or

Electron affinity is the energy charge that occurs when one mole of electrons is removed from mole of gaseous ion (anion) to form one mole of gaseous atoms



First electron affinity

The first electron affinity is the energy given out when one mole of electrons is added to one mole of gaseous atoms to form one mole of unipositively charged gaseous ion.

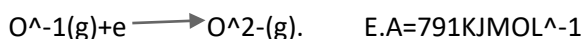


First electron affinity is always an exothermic process because the electron being added is always attracted by the nucleus thus heat is given out

The more exothermic the value of the house electron affinity the more stable the ion formed

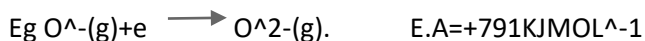
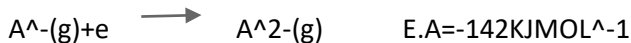
The negative ion produced by addition of electron now repels further electrons to be added so that to add a second electron is resisted and energy must be applied to effect it.

The second electron affinity is therefore positive ie endothermic



Definition

The second electron affinity is the energy absorbed when one mole of uninegatively charge gaseous ion to form one mole of dinegatively chared gaseous ion



Question

- i) define electron affinity ii) write the equation to show how first electron affinity of oxygen atom lines iii) explain why the process leading to first electron eis exothermic while that for the second electron affinity is endothermic Solution

Refer to notes





iii) the process leading to first electron affinity is exothermic because an electron which is negatively charged is added to the neutral atom hence there is less repulsion between the added electron and electron present

The second electron affinity is energy change from an endothermic process because an electron is added to a negative ion hence there is strong repulsion between the added electron and negative ion

Determination of the electron affinity is estimated by use of a bomb calorimeter cycle eg for a binary compound MX

Note

The more exothermic, the more negative the electron affinity the more stable is the anion

Therefore among the halogens, fluorine is the most stable.

ii) formation of a divalent ion is endothermic which shows that a univalent ion is more stable than a divalent one. **Factors**

**affecting electron affinity**

i) atomic radius (atomic size)

Electron affinity increases with decrease in atomic radius and vice versa

Atoms with small atomic radius have high effective nuclear charge or attraction such that the incoming electron is strongly attracted

For a large atomic radius nuclear attraction for the incoming electron is small

ii) screening effect

Electron affinity decreases with increase in screening effect.

This is because the screening effect reduces on the effective nuclear charge such that the incoming electron is less attracted by the nucleus hence the lower the electron affinity

The smaller the screening effect the more strongly attracted is the incoming electron and the greater the electron affinity.

**(Effective) nuclear charge**

Electron affinity increases with increase in nuclear charge and vice versa

The greater the nuclear charge the stronger is the incoming electron attracted and the greater is the electron affinity.

The smaller the nuclear charge the less strongly is the electron added attracted and the lower the electron affinity

**Variation of electron affinity down the group**

### Eg group (vii)

Element	F	Cl	Br	I
Electron affinity	-323	-364	-324	-295

Trend: electron affinity generally decreases down the group

### Explanation

Down the group both screening effect and nuclear charge increases but because of an extra energy level of electrons added the increase in screening effect outweighs that of nuclear charge so that the effective nuclear charge decreases

### Question

Use the above data to draw a graph of electron affinity versus atomic number

### Variation of first electron affinity across a period

#### Eg period 3

Elements	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic number	11	12	13	14	15	16	17	–
Electron affinity	-80	70	-35	-140	-70	-200	-370	0

### Trend

There is a general increase in first electron affinity from sodium to argon

### Explanation

Across the period atomic radius decreases nuclear charge increases and screening effect increases but since electrons are added to the same main energy level, the increase in nuclear is much more than screening effect.

As a result, the attraction for the incoming electron increases and therefore first electron affinity increases.

The first electron affinity of magnesium is higher than that of aluminum.

This is due to the electronic structure of magnesium and aluminum as below

Mg:  $1s^2 2s^2 2p^6 3s^2$

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

In magnesium the electron is added to an energy level that has a completely full 3s sub shell which is stable.

The electron experiences greater repulsion from the existing electrons than the nuclear attraction. In aluminum the 3p subenergy level has one electron and is unstable therefore the added electron experiences more attraction than repulsion.

The first electron affinity of phosphorus is less than that of sulphur.

Again this due to the electronic configuration

P:  $1S^2 2S^2 2P^6 3S^2 3P^3$

S:  $1S^2 2S^2 2P^6 3S^2 3P^4$

In phosphorus the electron is added to a Half filled 3p subenergy level which is energetically stable. Therefore the incoming electron experiences more repulsion than nuclear attraction the lower electrons affinity. In sulphur the electron is added to 3p subenergy level with 4 electron which is unstable. The element experiences more nuclear attraction than repulsion hence higher electron affinity.

The graph that shows variation of the first electron affinity of the elements in period 3 of the periodic table is as below  
ELECTRONEGATIVITY

Elements that tend to acquire electrons in their chemical interaction are said to be electronegative.

The electronegativity of an atom provides a numerical value of the power of that atom in a molecule that attracts electrons.

Definition

Electronegativity is the tendency of an atom to become negatively charged in it's covalent compounds.

Or

Electronegativity is the relative attraction of an atom for the electrons of a covalent bond formed with in an atom of another element.

Or

Electronegativity is the force of attraction between an atom and an electron separated by a distance equal to the radius of the atom

#### Variation of electronegativity accross a period eg Period 3

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.3	1.5	1.8	2.1	2.5	3.0

**Trend:** electronegativity increases across a period.

Explanation

In moving from left to right across a period from one element to the next atomic radius decreases both nuclear charge and screening effect increases. But since electrons are added to the same main energy level, the increase in nuclear charge outweighs the increase in screening effect. The atoms have an increasing nuclear power(nuclear attraction) hence an increase in electronegativity.

#### Variation of electronegativity down the group.eg. group VII

Element	Electronegativity
F	4.0

Cl	3.0
Br	2.8
I	2.5

### Trend

The electronegativity of an element decreases down the group. Down the group, both screening effect and nuclear charge increase but the increase in screening effect outweighs the nuclear charge due to an extra energy level of electrons which is added down the group. Therefore effective charge decreases and hence the atom develops a decreasing power to attract electrons.

### Factors that determine the magnitude of electronegativity of an element

#### 1. Atomic radius

Electronegativity increases with a decrease in atomic radius.

For a small atomic radius, the bonding electrons are nearer to the nucleus thus they experience a greater attraction. For a large atomic radius the bonding electrons are far away from the nucleus thus they experience less attraction.

#### 2. Nuclear attraction

Electronegativity value increases with increase in nuclear charge

For a low nuclear charge, the bonding electrons experience a low nuclear attraction leading to low electronegativity value

For high nuclear charge the bonding electrons experience a high nuclear attraction leading to high electronegativity.

#### Screening effect

Electronegativity increases with decrease in screening effect.

A low screening effect implies that bonding electrons are less effectively shielded from the nuclear charge thus they experience a higher attraction.

A high screening effect implies that the bonding electrons are effectively shielded from the nuclear charge thus they experience a less attraction leading to low electronegativity value

### ELECTROPOSITIVITY

This is the tendency of an element to lose its valence electrons to become positively charged Or

Is the measure of the ease with which the electrons of an element can be removed from an atom.

### Variation of electropositivity down the group who group 1V

Electropositivity decreases down the group.

#### Explanation

Down the group nuclear charge and screening effect of the inner electrons increases. However since a full energy level of electrons is added down the group, the increase in nuclear effect outweighs the increase in nuclear charge.

The atomic radius and the nuclear attraction for the valence electrons reduce. This increases the electropositivity of the element.

### **Variation of electropositivity across a period**

#### **Trend**

Electropositivity reduces across a period

#### **Explanation**

Across the period atomic radius decreases both the screening effect and nuclear charge increase.

Since the electrons are added to the same main energy level they shield each other poorly such that the increase in nuclear charge outweighs the increase in screening effect.

Thus nuclear attraction for the valence electrons increases across the period which leads to reduction in electropositivity.

### **DIAGONAL AND HORIZONTAL RELATIONSHIP**

#### **DIAGONAL RELATIONSHIP**

What is diagonal relationship

On moving diagonally across a periodic table elements show certain similarities.

These are usually weaker than similarities in the group.

The resemblance is more pronounced and indicated in the elements above.

Eg

In moving across a period the electronegativity increases while down the group decreases. Therefore in moving diagonally the electronegativity always remains constant. Elements and their compounds have similar properties along the diagonal called diagonal relationship

#### **Definition**

Diagonal relationship is the similarity in chemical properties between elements in period 2 to their diagonal neighbors in period 3 and the adjacent groups.

Eg lithium and magnesium

Beryllium and aluminum

Boron and silicon

## Why do elements show diagonal relationship These

elements show diagonal relationship because

i) they have similar electronegativity or positivity ii)

the cations have similar charge densities iii) their

atoms have similar standard electron potential

## Properties that show or illustrate diagonal relationship.(similarities between lithium and magnesium)

1. Their fluorides, phosphates, and carbonates are sparingly soluble in water

2. Both lithium and magnesium form normal oxides when burnt.



3. The oxy salts (hydroxides, carbonates and nitrates) of both magnesium and lithium are easily decomposed by heat.



4. Hydroxides of both lithium and magnesium are not deliquescent and are soluble in water 5. Both lithium and magnesium form nitrides when heated in air



6. Hydrogen carbonates of lithium and magnesium exist only in solution 7.

The halides of both lithium and magnesium are soluble in organic solvents.

8. The boiling points both lithium and magnesium are comparatively high.

Li has a b.p of 1336°C

Mg has a b.p of 1120°C

9. Both lithium and magnesium react with carbon to form ionic cyanides.



## Properties that show diagonal relationship or similarities between beryllium and aluminum

- Both beryllium and aluminum are rendered passive by concentrated nitric acid
- Both beryllium and aluminum and their hydroxides and oxides are amphoteric.

- Ions of both have strong tendency to form complexes
- Both react with concentrated solutions of alkali  $\square$  Carbides of both yield methane and hydrolysis
 
$$\text{Be}_2\text{C}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_4(\text{g}) + 2\text{BeO}(\text{s})$$

$$\text{Be}_2\text{C}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Be}(\text{OH})_2(\text{s}) + \text{CH}_2(\text{g})$$

$$\text{Al}_4\text{C}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \longrightarrow 3\text{CH}_4(\text{g}) + 2\text{Al}_2\text{O}_3(\text{s})$$
- Chlorides of both beryllium and aluminum are readily hydrolysed and exist as dimers (a process called dimerisation)  $\square$

Question

Why does aluminum and beryllium show diagonal relationship?

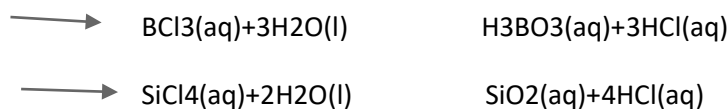
They show diagonal relationship because

- ★ Both atoms have similar electronegativity
- ★ Both ions have similar charge density

**Properties which boron and silicon show diagonal relationship**

**The properties are;**

1. Oxides of both are acidic and have giant covalent structures ( $\text{BO}_3$  and  $\text{SiO}_2$ )
2. Both form covalent compounds
3. Both are non-metals
4. Both give rise to covalent volatile hydrides eg  $\text{BeH}_6$  and  $\text{Si}_2\text{H}_6$
5. Both boron and silicon form chlorides which are hydrated to form acidic solutions.



Question

Explain the following observation

Beryllium belongs to group 11 in the periodic table and yet its chemistry and that of its compounds resemble that of aluminum.

Beryllium atom has a small atomic radius compared to the other atoms in group 11

This leads to low electropositivity, high charge density, high polarising power and high ionisation energy.

The charge density of  $\text{Be}^{2+}$  and  $\text{Al}^{3+}$  are similar. This makes their chemistry similar.

Explain the observation

Lithium is in group 1 in the periodic table but its properties resemble those of magnesium which is in group 2

Lithium and magnesium have diagonal relationship

They have the same electronegativity value (or electropositivity)

Their cations also have similar charge densities (or polarising power)

## NITROGEN AND PHOSPHORUS

Nitrogen differs from phosphorus in that nitrogen is gaseous and diatomic at room temperature. Nitrogen gas can be condensed with a liquid at room temperature.

It is triply bonded and very stable phosphorus is a solid at room temperature

The difference in physical states is due to the following

Nitrogen atom has a small atomic radius so it can form stable multiple bonds between nitrogen atoms yet phosphorus atom has a large atomic radius so it cannot form multiple bonds between phosphorus atoms.

Nitrogen forms discrete diatomic molecules yet phosphorus forms discrete tetra atomic molecules of structure.

Both molecules are held together by Vander waals forces.

The molecular mass of phosphorus molecule is greater than the molecular mass of nitrogen molecules.

The strength of Vander waals forces increase in molecular mass.

The strength in Vander waals forces between phosphorus molecules is greater than that between nitrogen molecules.

Because nitrogen molecules are very stable nitrogen doesn't react with acid and alkalis but phosphorus reacts with acids.

Eg phosphorus forms Penta chloride which nitrogen doesn't. Thus because phosphorus has the vacant d-orbitals

$1S^22S^22P^63S^23d^0$

Ammonia is more stable than phosphine(PH<sub>3</sub>).

Ammonium ion is more stable than phosphine. Ammonia is highly soluble in water to give an alkaline solution. Probably due to hydrogen bonding whereas phosphine is sparingly soluble in water and the solution is neutral because of very weak hydrogen bonding. The oxyacids of nitrogen are stronger than those of phosphorus. Thus nitric acid is stronger than orthophosphoric acid. Nitric acid is a strong oxidising agent yet orthophosphoric acid has no oxidising agent. **Nitrogen and phosphorus**

<b>Nitrogen</b>	<b>Phosphorus</b>
Gas at room temperature	Solid at room temperature
Has only one form	Has more than one form
Inert to most gases	Moderately reactive
Doesn't form pentachlorine	Forms a pentachloride
Has tripple bonds between it's atoms	Has single bonds between its atoms

**Explain the following observation.**

**2017 (c)**

Nitrogen is a gas at room temperature whereas phosphorus is a solid at the same temperature yet both of them belong to same group in the periodic table

COMPARISON OF OXYGEN AND SULPHUR



1. Oxygen is a gas at room temperature and exists as a diatomic molecule while sulphur is a solid at room temperature
2. Oxygen is more electronegative and forms more ionic compound than sulphur. This is why oxygen forms strong hydrogen bonds.
3. Oxygen has a covalency of 2 ie two covalent bonds can be formed with oxygen but sulphur has a covalency of 2,4 and 6 by using some of the d-orbitals. Oxygen lacks d-orbitals.
4. Oxygen forms stable double covalent bonds with itself and other elements more readily but sulphur is unable to form double bonds with in itself.