S.5 INORGANIC CHEMISTRY STUDY NOTES 2020

1 PERIODIC PROPERTIES.

1) ***Atomic Radius***.

Definition:

Is the distance of closest approach of one atom to another atom in a bonding situation.

Atomic radius is half the inter-nuclear distance between two identical atoms in a bonding situation.

At such a distance, the repulsive forces between nucleus-nucleus, electron-electron and the attractive forces between nucleus-electron just balance.

Trends in Atomic Radius I)

Across the period.

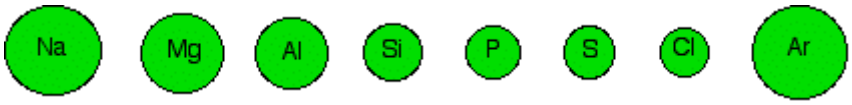
Atomic radius decreases across the period.

Explanation

- On traversing the period from one element to the next, the additional electron is added to shells with the same energy ie no new energy level is formed.
- The nuclear charge progressively increases and yet the screening/ shielding effect of the inner complete shells remains almost constant.
- As a result the effective nuclear charge increases and electrons in the outer most shell are pulled more strongly leading to a decrease in atomic radius.

Elements	At. Number	Electronic configuration
Li	3	$1S^2 2S^1$
Be	4	$1S^2 2S^2$
B	5	$1S^2 2S^2 2P^1$
C	6	$1S^2 2S^2 2P^2$
N	7	$1S^2 2S^2 2P^3$
O	8	$1S^2 2S^2 2P^4$
F	9	$1S^2 2S^2 2P^5$
Ne	10	$1S^2 2S^2 2P^6$

The diagram shows how the atomic radius changes as you go across Period 3.



The figures used to construct this diagram are based on:

metallic radii for Na, Mg and Al; covalent radii for Si, P, S and Cl; the

van der Waals radius for Ar because it doesn't form any strong bonds.

ii) Down the group

Atomic radius increases down the group in the periodic Table.

Explanation

- On descending any group from one element to the next, electrons are being added to shells with higher energies (i.e a new electron shell is formed)
- As a result both the nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge.

- The effective nuclear charge therefore decreases , nuclear attraction for the outer most electrons decreases hence increase in atomic radius.

Element	Atomic Number	Configuration
Li	3	$1S^2 2S^1$
Na	11	$1S^2 2S^2 2P^6 3S^1$
K	19	$1S^2 2S^2 2P^6 3S^2 3P^6 4S^1$
Rb	37	$1S_2 2S_2 2P_6 3S_2 3P_6 4S_2 3d_{10} 4P_6 5S_1$
Cs	55	--------

Cations

Cation is (a positive ion) formed by the removal of one or more electrons from an atom.
A cation is smaller than the atom from which its formed.

Explanation

After the removal of one or more electrons, the number of protons in the nucleus become greater than the number of remaining electrons, thus the proton-electron ratio increases.

As a result, the nuclear attraction for the remaining electrons increases leading to a decrease in cationic radius.

Anions

An anion (a negatively charged ion) is formed by gain of one or more electrons by an atom.
The radius of an anion is bigger than that of the corresponding atom from which its formed.

Explanation

After the gain of one or more electrons by an atom, the number of electrons present becomes more than the number of protons present in the nucleus thus the proton-electron ratio decreases.

The nuclear attraction for the many electrons now present decreases leading to increase in anionic radius.

Isoelectronic ions

Isoelectronic ions are ions that have the same number of electrons and the same electronic structure.

For example:

Isoelectronic ions	**number of electrons**
1. Al^{3+},Mg^{2+}, Na^{+}, F^{-}	10 electrons
2. S^{2-}, Cl^{-}, K^{+}, Ca^{2+}	18 electrons

isoelctronic ions, Al^{3+},Mg^{2+},Na^{+}, F^{-} (ions both have 10 electrons):

- Al^{3+} has 13 protons, a nuclear charge of +13.
- Mg^{2+} has 12 protons, a nuclear charge of +12.
- Na^{+} has 11 protons, a nuclear charge of +11.
- F^{-} has 9 protons, a nuclear charge of +9.

Al^{3+}, with the largest nuclear charge will be expected to have the greatest attraction of its electrons .

Therefore Al^{3+} has the smallest ionic radius i.e radius is in the order Al^{3+} <Mg^{2+} <Na^{+} <F^{-}

The radius decreases **as the positive nuclear charge increases. Consequently charge densities and polarizing powers of the ions increase.**

Look at the second example of isoelctronic ions, S^{2-}, Cl^{-}, K^{+}, Ca^{2+} (ions all have 18 electrons):

- S^{2-} has 16 protons, a nuclear charge of +16.

- Cl^- has 17 protons, a nuclear charge of +17.
- K^+ has 19 protons, a nuclear charge of +19.
- Ca^{2+} has 20 protons, a nuclear charge of +20.

2. *IONISATION ENERGY*

The **ionization energy** of an atom measures how strongly an atom holds its electrons.

Definition:

Ionization energy(1^{st} ionization energy) of an element is the minimum amount of energy required to remove an electron completely from the outer most shell of an isolated gaseous atom to form a unipositively charged gaseous ion.

$M_{(g)} \rightarrow M^+_{(g)} + e^-$ H= 1^{st} ionization energy.

Second ionization energy

Is the minimum amount of energy required to remove an electron from the outer most shell of a unipositively charged gaseous ion to form a dipositively charged gaseous ion.

$M^+_{(g)} \rightarrow M^{2+}_{(g)} + e^-$ H= 2^{nd} ionization energy.

The higher the value of the ionization energy, the more difficult it is to remove the electron.

As electrons are removed, the positive charge from the nucleus remains unchanged, however, **the ionization energy is higher for each subsequent electron**.

There is also a big increase in ionization energy for removal of an electron from an inner shell (lower *n* value).

This is due to the fact that when you move to an orbital with a lower principle quantum number, you are removing an electron which is much closer to the nucleus and is being strongly held by the nucleus.

FACTORS AFFECTING 1^{ST} IONIZATION ENERGY

1) **Nuclear charge of an atom.**

2) **Shielding / Screening effect of inner shells of electrons.**

3) **Atomic radius.**

4) **Electronic configuration of the outer shell**.

Explanation

1. Nuclear charge.

- ✓ When the nuclear charge is high, the electrons present in the outer most shell are attracted more strongly by the nucleus.
- ✓ Therefore removing an electron from this shell requires more energy leading to high 1^{st} ionization energy.
- ✓ When the nuclear charge is low, the electrons present in the outer shell are attracted less strongly by the nucleus.
- ✓ Therefore removing an electron from it requires less energy leading to low 1^{st} ionization energy.

2. Shielding effect of inner complete shells of electrons.

- This is the tendency of the inner electrons to screen the other outer electrons from the nuclear attraction.
- When the screening effect is high, the effective nuclear charge for the outer most electrons reduces.
- As such less energy is required to remove an electron from the outer most shell leading to low 1^{st} ionization energy.
- When the screening effect is low, the effective nuclear charge for the outer most electrons increases.

As a result more energy is required to remove an electron from this outer shell against a high nuclear attraction.

3. Atomic radius.

- If the atomic radius is small, the outer most electrons are closer to the nucleus and are attracted more strongly by it. Thus removing an electron from this outer shell requires more energy leading to high 1^{st} ionization energy.

- If the atomic radius is large, the outer most electrons are more distant from the nucleus. There is less attraction from the nucleus, and an electron can be removed easily leading to a low 1^{st} ionization energy.

4. Electronic configuration of the outer most shell.

- ✓ When the first electron is coming from an outer sub-shell which is half full (eg. N: $1S^2 2S^2 2P^3$), a lot of energy is needed since the unpaired electrons experience minimum repulsion and the shell is thermodynamically stable.

- ✓ When the 1^{st} electron is coming from an outer shell which is fully filled e.g Ne: $1S^2 2S^2 2P^6$,a lot more energy is needed to remove it because the shell is thermodynamically more stable.

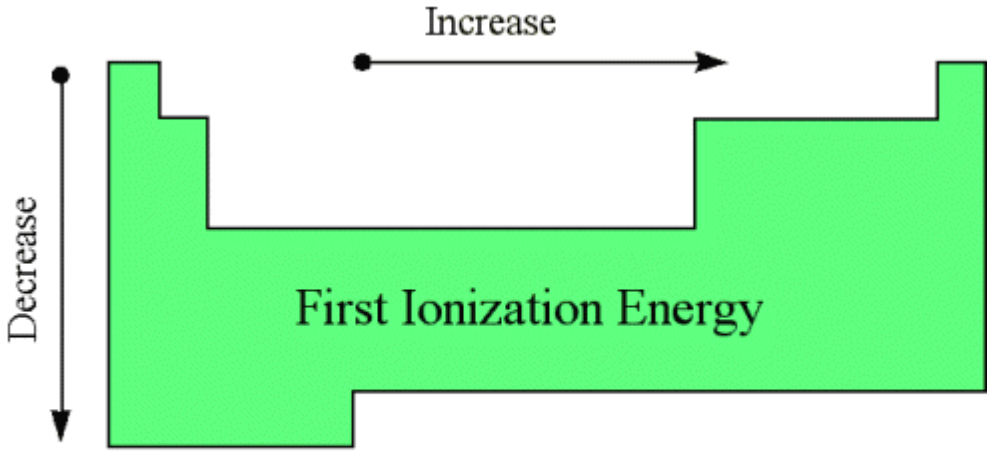
- ✓ When the 1^{st} electron comes from a shell where electron pairing has begun e.g O:($1S^2 2S^2 2P^4$), less energy is required because of mutual repulsion between paired electrons.

Periodic trends in ionization energies

First ionization energies as a function of atomic number

Within each period (row) the 1^{st} ionization energy typically increases with atomic number

Within each group (column) the 1^{st} ionization energy typically decreases with increasing atomic number



General trends for the energy required to remove the first electron (first ionization energy) of an element

The basis for these observations:

As the effective charge increases, or as the distance of the electron from the nucleus decreases, the greater the attraction between the nucleus and the electron.

The effective charge increases across a period, in addition, the atomic radius decreases

As we move down a group the distance from the nucleus increases and the attraction of the electrons for the nucleus decreases.

a) 1st ionization energy generally increases across the period in the periodic Table.

Explanation

On traversing any period in the periodic Table from one element to the next, electrons are being added to shells with the same energy as such the nuclear charge progressively increases while the screening effect of the inner shells remains almost constant.

Consequently, the effective nuclear charge increases leading to a high nuclear attraction for the outer most electrons. Thus removing the 1st electron requires more energy.

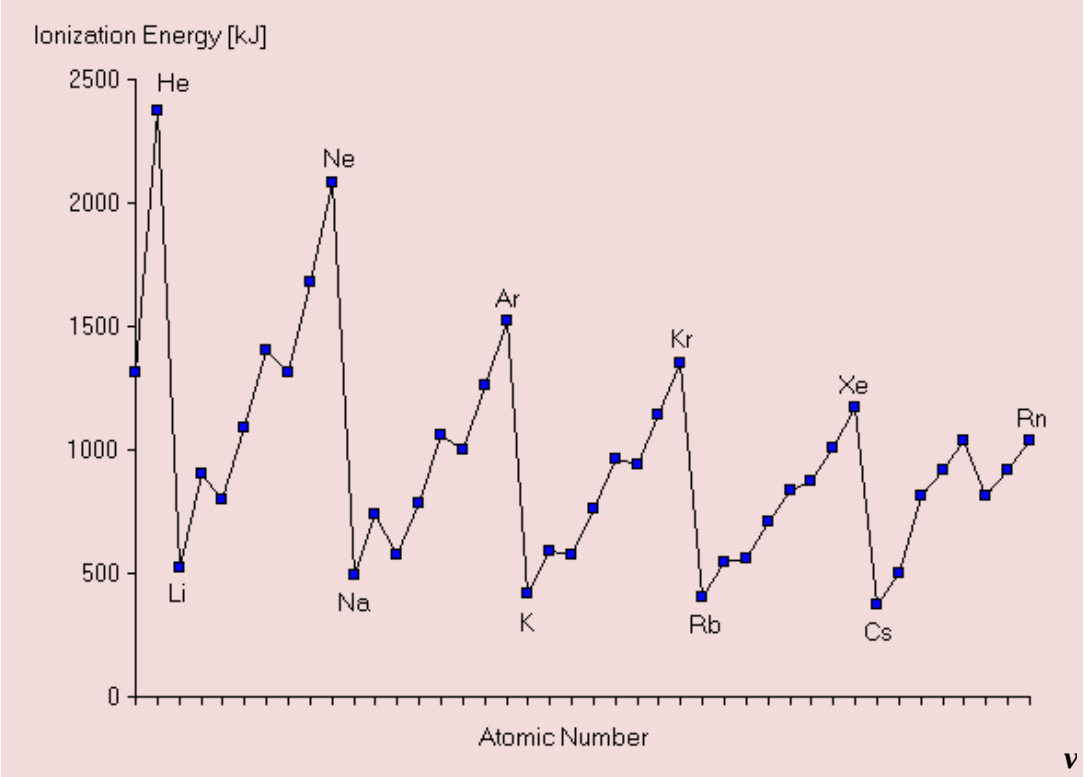
b) 1st ionization energy generally decreases down any group in the periodic Table.

Explanation

On descending any group from one element to the next in the periodic table, electrons are being added to shells with higher energy i.e an extra shell of electrons is added.

Thus both the nuclear charge and the screening effect increase but the increase in screening effect out- weighs that due to nuclear charge.

The effective nuclear charge progressively decreases leading to a decreased nuclear attraction for the outer most electrons hence 1st ionization energy decreases.



Explanation

- ✓ On traversing the short period, lithium to neon, the 1st ionization energy increases in general but there is a break observed at boron and oxygen.
- ✓ Lithium, $1S^2 2S^1$ has the lowest 1st ionization energy . This is because the single electron in the outer most 2s shell is weakly held by the nucleus due to the shielding effect of complete inner 1s-electrons.

- ✓ Beryllium, $1S^2 2S^2$ has a higher 1^{st} I.E because the nuclear charge increases whilst the electron is being added to the same 2s shell. Above all the outer most 2s shell is full.

- ✓ Boron , $1S^2 2S^2\ 2p^1$ loses the outer most p-electron easily despite an increase in the nuclear charge because the shielding effect of the interposing complete inner s-shells increases thus reducing the effective nuclear charge considerably. In addition, the 2p sub-shell is further from the nucleus than the 2s electron that is removed from Be (1^{st} I.E of Be > for B).

- ✓ There after the nuclear charge increases from boron through carbon $1S^2 2S^2 2P^2$ to nitrogen $1S^2 2S^2 2P^3$, in line with an increase in nuclear charge while electrons are being added to the same shell.

- ✓ At nitrogen, the 2p-subshell is half full, the three electrons being unpaired experience minimum repulsion thus thermodynamically stable.

- ✓ In the case of oxygen $1S^2 2S^2 2P^4$,electron is being paired in one of the 2p-orbitals as such there is mutual repulsion between the two paired electrons. An electron can easily be removed from this outer 2p-shell thus a decrease in 1^{st} I.E is observed.

- ✓ Further increase in ionization energy is observed on traversing the period from oxygen to neon. This is in line with increase in nuclear charge as the 2p shell is building up and reaches a maximum at neon, $1S^2 2S^2 2P^6$, which has a complete stable configuration.

A similar trend is observed on traversing the 2^{nd} short period from sodium to argon.

NB:

In every period, noble gases have the highest 1^{st} ionization energy. This is because noble gases have fully filled outer most shell thus thermodynamically stable.

Helium : $1s^2$ has the highest 1^{st} ionization energy of all atoms.

This is because Helium atom has the smallest atomic radius therefore electrons in its outer most shell are closer to the nucleus and are attracted more strongly.

Also it has a stable outer most shell $1s^2$.

IMPORTANCE OF IONIZATION ENERGY

Ionization energy provides a basis for understanding the chemistry of an element. The following information is provided:

1. Atomic number of the element .

This is given by the number of successive ionization energies an atom has got e.g sodium with 11 successive ionization energies has atomic number 11.

2. The arrangement of electrons in the shells.

A plot of successive ionization energies of calcium shows distinct portions.

Qn.

Element	1^{st} I.E	2^{nd} I.E	3^{rd} I.E	4^{th} I.E
A	800	2400	3700	25000
B	900	1800	14800	21000
C	500	4600	6900	9500
D	1090	2400	4600	6200
E	1310	3400	5300	7500

The table below shows the 1^{st} four ionization energies of elements A-E.

a) Which group in the periodic table does each of the following elements belong: i)

A ii) B iii) C

Give a reason for your answer in each case.

Qn.

Element	A	B	C	D	E	F
1^{st} I.E	1013	1000	1255	1519	418	590
2^{nd} I.E	1904	2255	2297	2665	3067	1146
3^{rd} I.E	2916	3389	3853	3933	4393	4916

The table below shows the successive ionization energies of elements A-F.

a) Which element is a noble gas? Give reason for your answer.

b) Which element belongs to :

i) group(i) ii) group(ii).

Give reason for your answer in each case.

Qn.

The table below shows the 1^{st} five ionization energies in K/J per mole for elements W-Z.

Element	1_{st}	2^{nd}	3^{rd}	4^{th}	5^{th}
W	577	1816	2745	11575	13251
X	738	1450	7730	10550	12756
Y	495	4563	6912	9540	11936
Z	1255	2297	3849	5163	13989

a) Identify the group to which each of the elements belong and give a reason for your answer in each case.

b) Which pair of elements will form :

i) an ionic bond between them?

ii) a covalent bond?

Qn.

The first 8 ionization energies in K/J per mole of an element Y are shown below:

1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}	6^{th}	7^{th}	8^{th}
786	1580	3230	4360	16000	20000	23600	29100

Which group in the periodic table does element Y belong? Give a reason for your answer.

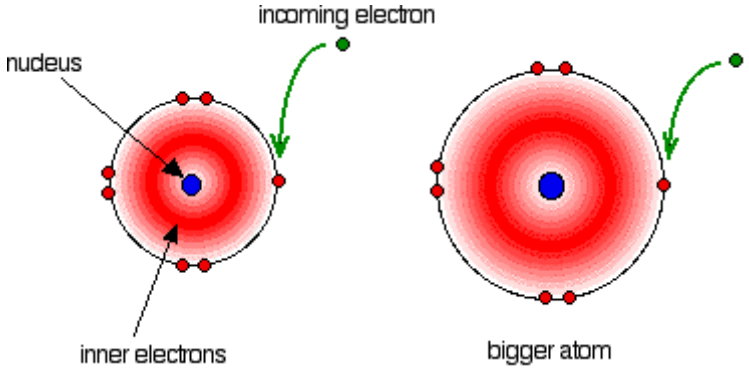
3. ELECTRON AFFINITY

Non-metallic electronegative elements accept electrons to form anions with a noble gas like structure as such the concept of electron affinity is more useful or important than ionization energy.

Electron affinity is defined as the enthalpy change that occurs when a gaseous atom gains an extra electron to form a univalently charged gaseous anion.

$\mathbf{M_{(g)} + e \rightarrow M^-_{(g)}}$ $\mathbf{\Delta H = 1^{st}}$ **Electron Affinity**.

The electron affinity is a measure of the attraction between the incoming electron and the nucleus. The higher the attraction, the higher the electron affinity.



First electron affinity:

of an element is defined as the energy released when a gaseous atom gains an extra electron to form a univalently charged gaseous anion.

$X_{(g)} + e \rightarrow X^-_{(g)}$ **H=△1st electron affinity**

After the gain of an electron by a gaseous atom, the negatively charged gaseous ion formed repels any further electron. **Second electron affinity**

is defined as the amount of energy absorbed/ required when a univalently charged gaseous anion gains an electron to form a divalently charged gaseous anion.

$X^-_{(g)} + e \rightarrow X^{2-}_{(g)}$ H=2nd△ electron affinity

First electron affinity is an exothermic process .

Explanation:

This is because the incoming electron experiences a greater attraction from the nucleus than repulsion from the electrons already present .

Second electron affinity is an endothermic process.

Explanation:

This is attributed to greater repulsive force which the electron being added experiences from electrons already present than the attraction from the nucleus, thus work must be done to over come the effect of repulsion. This work involves input of heat energy.

Note:

Because of the same reason, the 3^{rd} ,4^{th} ,5^{th} etc electron affinity will have a positive H △sign.

FACTORS THAT DETERMINE THE VALUE OF 1st E.A

1**. Nuclear charge.**

2. Atomic radius.

3. Shielding/ screening effect of the inner complete shells of electrons.

4. Electronic configuration of the outer shell of an atom.

Explanation

1. Nuclear charge

If the nuclear charge is high, the nuclear attraction for the incoming electron will be high. As the atoms gains the electron, a lot of energy is released.

If the nuclear charge is low, the attraction for the incoming electron will be low leading to a low electron affinity.

2. Atomic radius

If the radius of an atom is small, the incoming electron experiences a high attraction from the nucleus of the atom. As such a lot of energy is given out as the atom gains the electron giving rise to a high electron affinity.

If the radius of an atom is large, the incoming electron experiences a weak attraction from the nucleus of the atom. As such a lot of energy is given out as the atom gains the electron giving rise to a high electron affinity.

3. Shielding effect of the electrons in the inner shells.

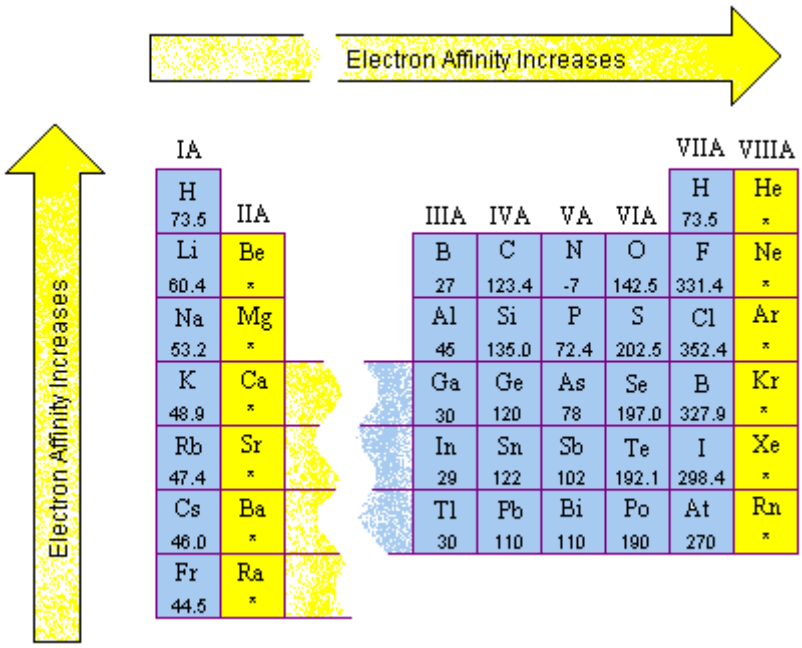
If the screening effect of the electrons in the inner shells is high, electron being added experiences a low attraction from the nucleus leading to a low value of electron affinity.

However, if the screening effect is low, the incoming electron experiences a high attraction from the nucleus leading to a large value of electron affinity.

4. Electronic configuration of the outer shell.

If an electron is being added to an atom with a stable outer electronic configuration (i.e half full or fully filled sub shell), the addition will not occur easily leading to a low value of electron affinity.

Variation of electron affinity



i) Across the period.

First electron affinity generally increases on traversing any period in the periodic table.

Explanation:

In moving across from one element to the next, electrons are being added to the shells with the same energy as a result the nuclear charge progressively increases while the screening effect of the electrons in the inner shells remains almost constant.

The effective nuclear charge increases leading to increased nuclear attraction for the electron being added and hence an increase in 1^{st} E.A.

ii) Down the group.

On descending any group in the periodic table, the electron affinity decreases.

Explanation.

In moving down the group from one element to the next, electrons are being added to shells with higher energy levels i.e an extra shell is created.

Both the nuclear charge and shielding effect increase but the increase in shielding effect is more rapid and outweighs that due to nuclear charge as such effective nuclear charge decreases.

Thus electron being added experiences a weaker attraction from the nucleus leading to a decrease in 1st E.A

1st ELECTRON AFFINITY OF HALOGENS

Element	1st E.A
Fluorine	-328
Chlorine	-349
Bromine	-325
Iodine	-295

Trend

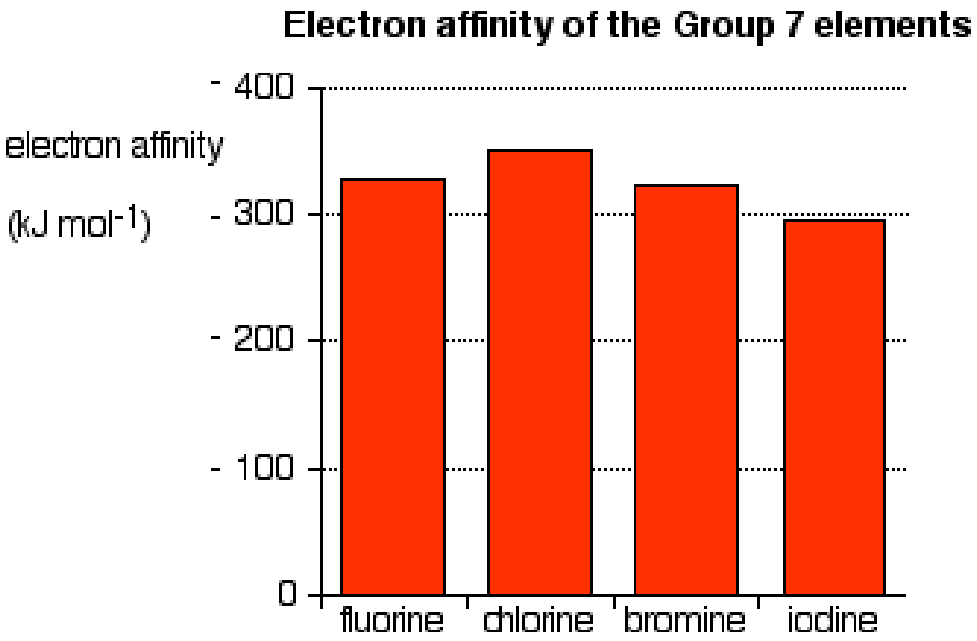
The E.A decreases numerically from Chlorine to Iodine.

As the atomic radius increases down the group, the screening effect of the inner complete shells of electrons increases too.

As such the electron being added experiences a weaker attraction from the nucleus leading to a decrease in 1st E.A.

Fluorine ,however, has a low value for its electron affinity, numerically less than that for chlorine.

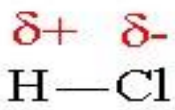
This is due to very small atomic radius of fluorine atom, the 7 electrons in the outermost shell are much closer to each other that they repel each other strongly hence the electron being added experiences a great repulsive force from the electrons already present.



Electronegativity

"the power of an atom in a molecule to attract electrons to itself".

- Linus Pauling



Chlorine is more electronegative than hydrogen.
The pair of electrons in the H-Cl bond are pulled toward the Cl giving it a partial negative (-) charge. The H has less electron density and has a partial positive (+) charge.
The symbol delta (δ) indicates a partial charge.

Electronegativity:

is the tendency of an atom in a covalent bond to attract/pull the bonding electrons more towards itself thereby creating partial charges.

FACTORS THAT DETERMINE ELECTRONEGATIVITY VALUES

1. Nuclear charge.

2. Atomic radius.

3. Screening effect of inner electrons.

Explanation

1. Nuclear charge.

If the nuclear charge of an atom covalently bonded to another atom is high, the nuclear attraction for the bonding electrons will be greater leading to a high electronegativity value.

If the nuclear charge is low, the attraction for the bonding electrons will be weaker leading to a low electronegativity value.

2. Atomic radius.

If the radius of an atom is small, the bonding electrons are nearer to the nucleus and as such experience a high nuclear attraction from the electronegative atom leading to a high electronegativity value.

If the atomic radius is large, the bonding electrons are far from the nucleus and as such experience a weak attraction from the nucleus leading to a low electronegativity value.

3. Shielding effect of the electrons in the inner shells.

If the screening effect of the electrons in the inner shells is high, the electrons in the covalent bond experience a low attraction from the nucleus leading to a low value of electronegativity.

However, if the screening effect is low, the electrons in the covalent bond experience a high attraction from the nucleus leading to a large value of electronegativity .

VARIATION IN ELECTRONEGATIVITY

Period 3:

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

a) Across the period, electronegativity increases from one element to the next.

Explanation:

As one traverses a period from one element to the next , additional electron is added to shells with the same energy.

As such the nuclear charge increases progressively while the screening effect of the inner complete shells of electrons remains almost unchanged.

As a result, the effective nuclear charge increases leading to increased nuclear attraction for the electrons in the covalent bond and hence increase in the electronegativity.

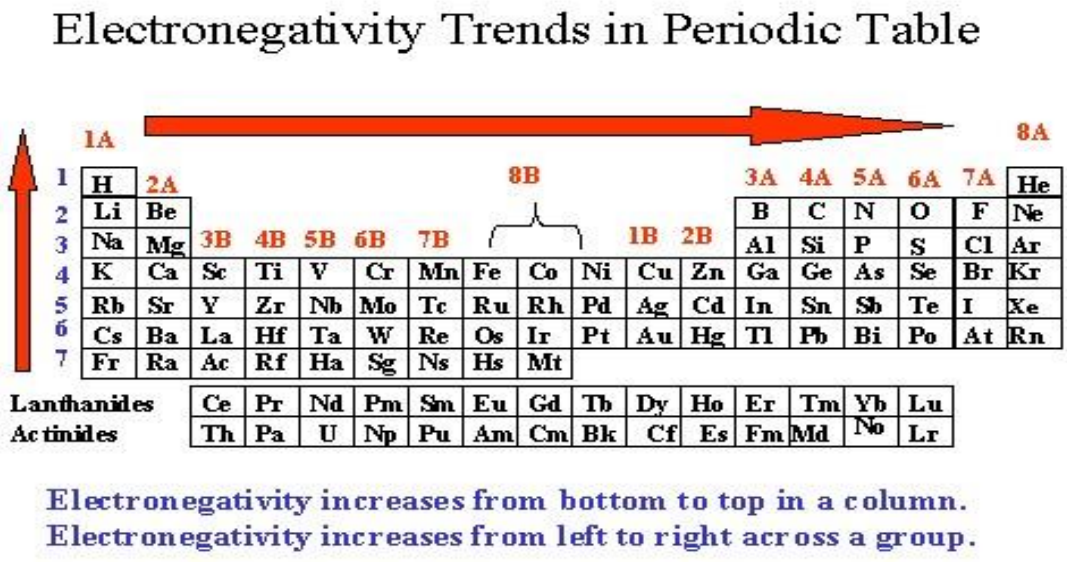
b) Down the group electronegativity generally decreases .

Group7

Element	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5

On descending any group in the periodic table from one element to the next, the screening effect of the inner complete shells of electrons out-weighs the increase in the nuclear charge due to an extra shell added.

The effective nuclear charge decreases as such the attraction for the electrons in the covalent bond decreases leading to a decrease in electronegativity.



ELECTROPOSITIVITY

This is the tendency of an atom to lose one or more electron(s) from its outer most shell to form a positively charged ion.

Electropositive elements are those which easily lose one or more electrons to become positively charged ions. E.g Na, Mg, Ca, K, Rb, Ba etc.

FACTORS THAT AFFECT ELECTROPOSITIVITY

1. Atomic Radius

2.Nuclear Charge

3.Shielding effect of the inner complete shells.

4.Electronic configuration.

Explanation:

1. **Atomic radius**

If the radius of an atom is small, the outer most electrons are nearer to the nucleus and experience a high nuclear attraction. Its then not easy for an atom to lose electrons leading to a decrease in electro positivity.

If the radius of an atom is large, the outer most electrons are far from the nucleus and experience a weak nuclear attraction and as a result they can easily be lost leading to an increase in electro positivity.

2. **Nuclear charge**

When the nuclear charge is high, the electrons in the outer shell are attracted more strongly as such removing an electron is difficult leading to a decrease in electro positivity.

When the nuclear charge is low, the electrons in the outer most shell are attracted less strongly as such removing an electron is relatively easy leading to an increase in electro positivity.

3. **Shielding effect of inner complete shells**

When the shielding effect of the inner complete shells is high, the effective nuclear charge decreases as such electrons in the outer most shell are less attracted to the nucleus. Removal of these electrons is easy leading to increase in electro- positivity.

When the screening effect is low, the effective nuclear charge increases as such electrons in the outer most shell are attracted more strongly to the nucleus. Removal of these electrons is difficult leading to a decrease in electro positivity.

4. **Electronic configuration**

If the outer most shell is fully or half filled, it is thermodynamically stable and an electron can not easily be lost leading to a decrease in electro positivity.

However, when electron pairing begins in one of the orbitals, the paired electrons experience mutual repulsion between them thus can easily be lost leading to an increase in electro positivity.

Variation of electro positivity

a) Electro positivity increases in moving down the group in the periodic table.

Explanation:

Down any group in the periodic table ,the increase in the screening effect out-weighs that due to nuclear charge due to an extra shell of electrons added from one element to the next.

This decreases the effective nuclear charge as a result the attraction for the outer most electrons reduces hence they can easily be lost leading to an increase in electro positivity.

b) Electro positivity decreases in moving across the period

Explanation

Across the period, the nuclear charge progressively increases while the screening effect of the inner complete shells remains almost unaltered from one element to the next as additional electron is added to shells with the same energy .

This increases the effective nuclear charge as such electrons in the outer most shell are attracted more strongly leading to increase in electro positivity.

MELTING POINT

Melting point is the constant temperature at which the pure solid and liquid phases of a substance co- exist in equilibrium at a given pressure.

FACTORS THAT DETERMINE MELTING POINT

a) metals

The melting points of metals depend on the following factors:

1. The number of electrons available for metallic bonding(delocalized electrons).

The greater the number of electrons contributed for metallic bonding the stronger the bond and the higher is the melting point.

2. The atomic radius.

When the radius of a metallic atom is small, the bonding electrons are attracted more strongly by the nucleus making the inter-atomic (element-element) bond length to be shorter and stronger thus high melting point.

When the radius of a metallic atom is large, the metallic bonding electrons are weakly attracted by the nucleus as a result the element-element bond becomes longer and weaker leading to a low melting point.

3. The crystal structure of the element.

b) Non-metals(molecular substances)

Melting points of non-metals depend on:

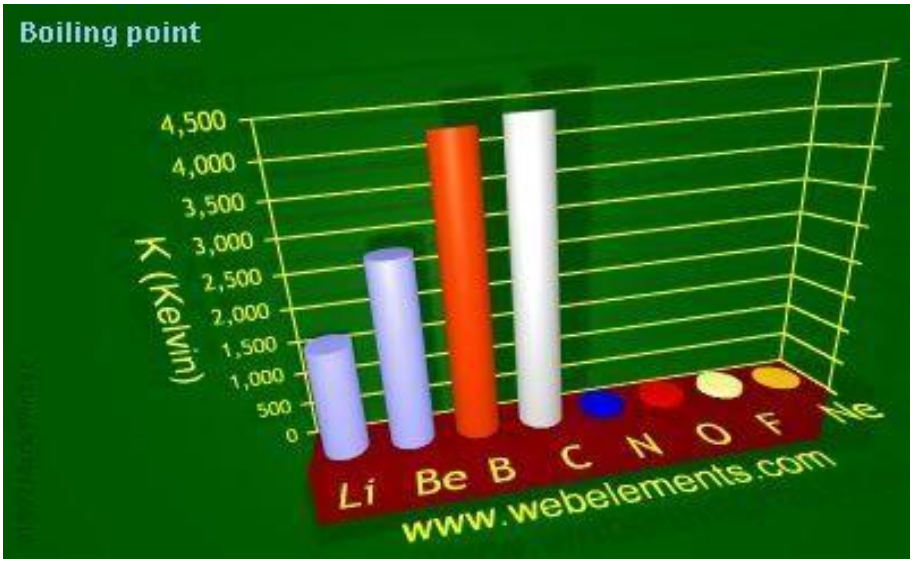
- Molecular mass
- Shape of molecules
- Type of intermolecular forces of attraction.

Trends in melting points/boiling points across period 2

(Li, Be, B, C, N, O, F, Ne)

Observation:

The Melting point of elements in period 2 increases from lithium to carbon and then decreases abruptly for the non metals nitrogen to neon.



Explanation

The increase in melting point or boiling point from Li to C is attributed to:

- Increase in number of electrons available for metallic bonding.

(1 for Li, 2 for Be, 3 for B & 4 for C)

The greater the electrons available, the stronger the bond and the higher the melting point.

- Decrease in atomic radius from Li to C.

The smaller the atomic radius, the closer are the bonding electrons to the nucleus and thus the shorter and stronger are the metallic bonds.

Change in the crystal structure of the elements across the period.

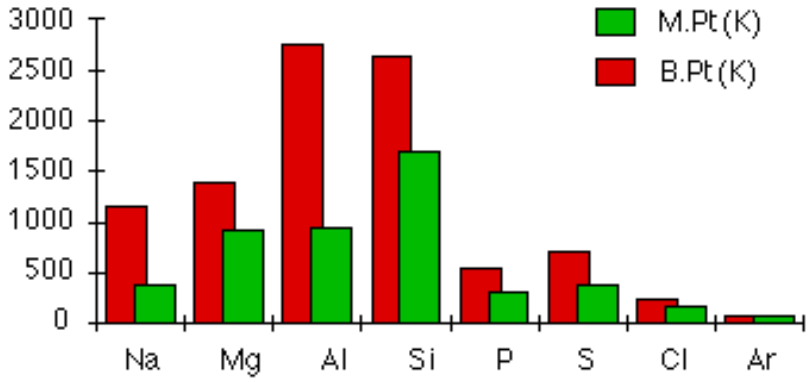
Li has a body centred cubic (b.c.c) structure which has its atoms less efficiently packed than Be with hexagonal closed packed (h.c.p).

Boron and carbon have giant (macro-) molecular structure composed of large number of covalently bonded atoms with carbon atoms more strongly bonded than boron.

However, the non metallic elements form simple molecular structures held by weak van der Waals forces of attractions as such have very low melting points.

TRENDS IN MELTING POINTS ACROSS PERIOD 3

The chart shows how the melting and boiling points of the elements change as you go across the period. The figures are plotted in Kelvin rather than °C to avoid having negative values.



The melting points increase from Na to Si and drops abruptly for the non metallic elements phosphorus to argon.

Melting and boiling points rise across the three metals because of the increasing strength of the metallic bonds.

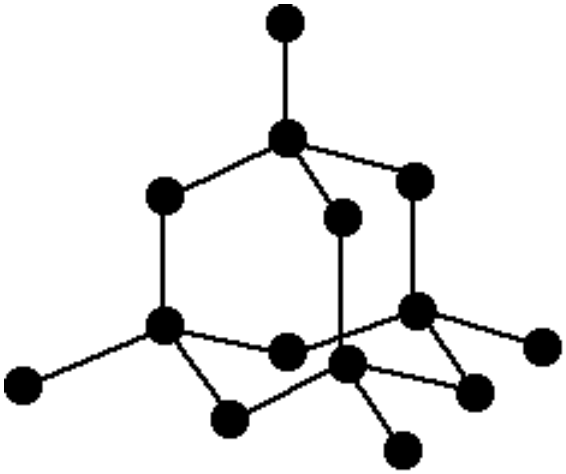
The number of electrons which each atom can contribute to the metallic bonding increases.

The atoms also get smaller(atomic radius decreases) as you go from sodium through magnesium to aluminium.

The nuclei of the atoms are getting more positively charged and the bonding electrons are getting progressively nearer to the nuclei and so more strongly attracted.

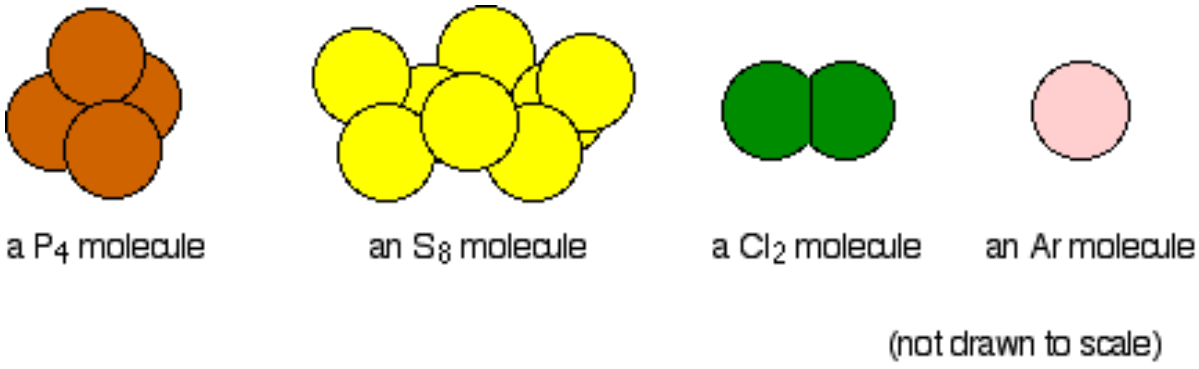
Silicon has the highest melting and boiling points because it has a giant covalent structure.

Here strong covalent bonds have to be broken before it melts or boils.



Phosphorus, sulphur, chlorine and argon have simple molecular structures held by weak van der Waals forces of attractions . Thus their melting points are much lower.

The melting and boiling points of non metals are governed entirely by the sizes of the molecules.



Phosphorus

Phosphorus contains a smaller P_4 molecules. To melt phosphorus you don't have to break any covalent bonds - just the much weaker van der Waals forces between the molecules.

Sulphur

Sulphur consists of a larger S_8 rings of atoms. The molecules are bigger than phosphorus molecules, and so the van der Waals forces of attractions will be stronger, leading to a higher melting and boiling point.

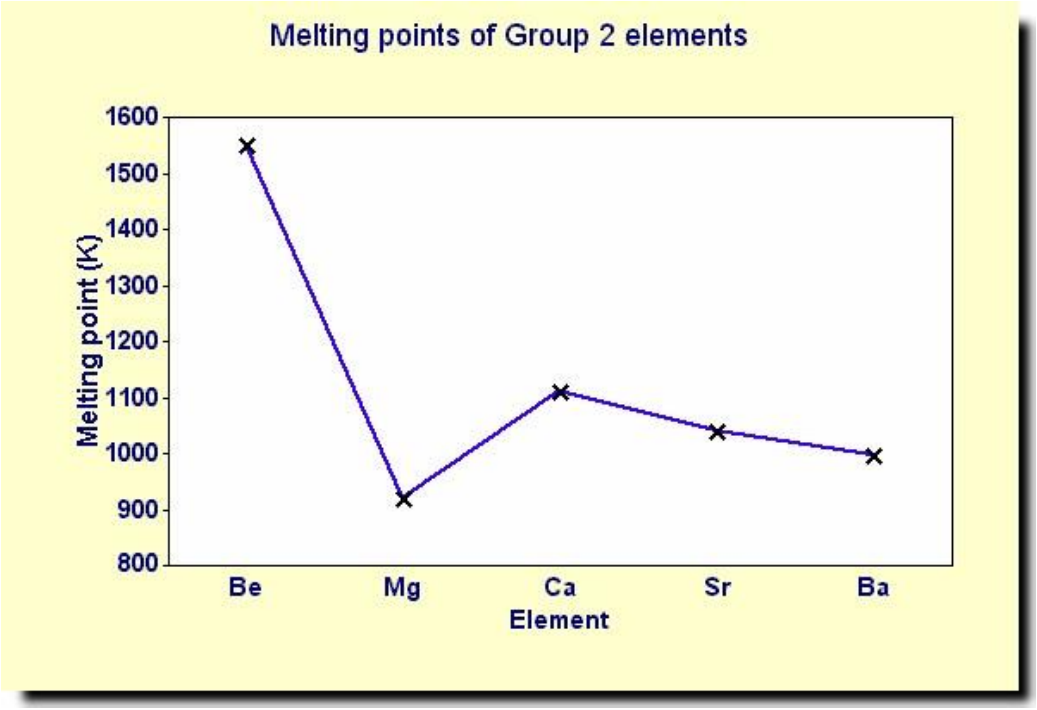
Chlorine

Chlorine, Cl_2, is a much smaller molecule with comparatively weak van der Waals forces of attractions, and so chlorine will have a lower melting and boiling point than sulphur or phosphorus.

Trend in melting points of Group 2 elements

The melting and boiling points of g it's roup 2 metals are higher than those of corresponding group 1 elements.

Graph of physical data



Explanation of this trend

Melting points generally **decrease** going **down** Group 2.

- The Group 2 elements are all metals with metallic bonding. In metallic bonding, metal cations in a metal lattice are attracted to delocalized electron.
- Therefore going down Group 2:
- the number of delocalized electrons remains the same .
- the charge on each metal cation stays the same at +2, but..
- the atoms become larger so that the positive nucleus gets further away from the delocalized electrons...

so the force of attraction between the delocalized electrons and the metal cations decreases.

Although in general the melting point decreases going down the group, the melting point for magnesium is anomalously low.

This is because magnesium has a different metallic structure from the other elements in the group apart from Be:

beryllium and magnesium have a hexagonal close-packed structure (h.c.p)

calcium and strontium have a face-centred cubic structure (f.c.c) and

barium has a body-centred cubic structure (b.c.c).

2. SOLUBILITY OF IONIC SALTS

Solubility of ionic salts in water is governed by two energy terms:

I. *Lattice energy,*

II. *Hydration (solvation) energy*. **Lattice energy**

is the amount of energy required to break 1 mole of an ionic salt into its constituent gaseous ions at standard conditions.

$NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$ ΔH = Lattice energy

Or

Lattice energy

is the amount of energy released when 1 mole of an ionic salt is formed from its constituent gaseous ions at standard conditions.

$Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(s)}$ ΔH = Lattice energy.

Hydration energy

is the amount of energy released when 1 mole of gaseous ions is fully dissolved in water at a given temperature.

$Na^{+}_{(g)} + aq \rightarrow Na^{+}_{(aq)}$ ΔH = Hydration energy.

Hydration energy has a negative sign because it involves attraction between a charge and water molecule which releases energy.

NB:

1. Each ion has its own hydration energy.

$Mg^{2+}_{(g)} + aq \rightarrow Mg^{2+}_{(aq)}$ $\quad H^{\theta}_{Hyd(298k)} = -696kj/mol.$

$Na^{+}_{(g)} + aq \rightarrow Na^{+}_{(aq)}$ $\quad H^{\theta}_{Hyd(298k)} = -406kj/mol.$

$Cl^{-}_{(g)} + aq \rightarrow Cl^{-}_{(aq)}$ $\quad H^{\theta}_{Hyd(298k)} = -377kj/mol.$

Therefore the $H^{\theta}_{Hyd(298k)}$ of NaCl = (-406 + -377) = -783kj/mol and that of $MgCl_2$ = (696 + 2x-377)= -1450.

The smaller the ionic radius the higher the charge density and so the greater(more negative) the hydration energy.

2. Water is a suitable solvent for dissolving ionic salts because:

- it is a polar solvent,
- has a high dielectric constant.
- has a large dipole moment, so that ion-dipole interaction is high.

If the solvation energy of a substance is greater than its lattice energy, the substance will dissolve exothermically in the solvent.

If the solvation energy is less than the lattice energy then the substance dissolves endothermically.

However, if lattice energy is much larger than hydration energy then the salt does not dissolve in water.

$H_{solution}$ is defined as the heat change that occurs when 1 mole of an ionic salt is fully dissolved in water at a given pressure.

$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ ΔH = Enthalpy of solution.

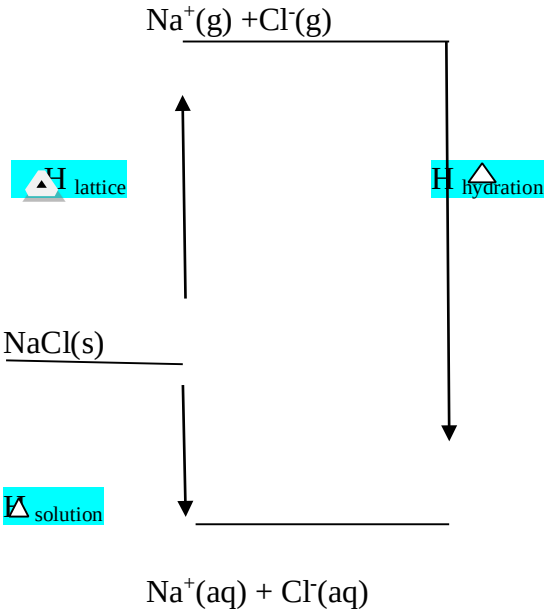


Figure shows Born-Haber cycle for solubility of NaCl.

$\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{hydration}$

NB:

Whenever this formula is being applied in calculation, the value of $\Delta H_{lattice}$ must be positive. This is because the formula is only valid when the salt is being decomposed as shown in the cycle above.

Qn1.

The lattice and hydration energies of $MgCl_2$ are -2644 kj/mole and -2653 kj/mole respectively.

i) Draw an energy diagram/ *Born-Haber cycle* for the solubility of $MgCl_2$ and indicate the energy changes that occur.

ii) Calculate the enthalpy of solution of the salt.

Qn2.

i) Using potassium iodide, draw an energy diagram/ Born Haber Cycle to show the energy changes during solubility of an ionic salt in water.

ii) The enthalpy of solution and lattice energy of potassium iodide are +21kj/mol and 642kj/mol respectively. Calculate the hydration energy for potassium iodide.

Factors that affect lattice energy

- Ionic charge (charge on the ion e.g Na^{+}, Mg^{2+}, Al^{3+})
- Ionic radius (distance between the ions)
- Crystal structure of a compound.

Explanation

Lattice energy is directly proportional to the ionic charge.

- ✓ If ionic charge is large, the electrostatic forces of attraction between the opposite charges is stronger leading to a high lattice energy.
- ✓ If ionic charge is small, the electrostatic forces of attraction between the opposite charges is weaker leading to a low lattice energy.

Lattice energy is inversely proportional to ionic radius.

- ➢ If ionic radius is large, the electrostatic forces of attraction between the opposite charges is weaker leading to a low lattice energy.
- ➢ On the other hand if the distance between the ions is small, the electrostatic forces of attraction between the opposite charges is greater leading to a high lattice energy.

Variation in Lattice & Hydration energies

a) Both lattice and hydration energies increase across the period.

Explanation

Across the period, the radius of ions become increasingly smaller and as such the charge density increases.

This implies that an ion is easily hydrated and also exerts a stronger electrostatic forces of attraction.

b) Both lattice and hydration energies decrease on descending the group.

Explanation.

Down the group, the radius of ions become increasingly larger. As such the charge density decreases and the ion is less hydrated and also exerts a weaker electrostatic forces of attraction.

3. DIAGONAL RELATIONSHIP

A relationship within the periodic table by which certain elements in the second period have a close chemical similarity to their diagonal neighbours in the next group of the third period.

This is particularly noticeable with the following pairs.

- Lithium and Magnesium: ○ Beryllium and Aluminium:
- Boron and Silicon

Causes of diagonal relationship:

I. Similar electro negativities,

II. Similar atomic & ionic radius ,

III. Similar hydration energies,

IV. Similar electrode potentials,

V. Similar charge densities & similar polarizing powers,

VI. Similar electropositivities.

Resemblance between Li & Mg

(1) Both react directly with nitrogen to form nitrides on heating.

$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$

$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

(2) Both react with oxygen gas to form normal oxides only.

$4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

(3) Both their nitrates decompose on heating to form normal oxide, nitrogen dioxide and oxygen gas.

$4LiNO_3(g) \rightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$

$2Mg(NO_3)_2(g) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$

(4) both form carbonates that decompose on heating.

$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$

$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

(5) Both react with carbon when heated to form ionic carbide.

$4Li(s) + C(s) \rightarrow Li_4C(s)$

$2Mg(s) + C \rightarrow Mg_2C(s)$

(6) Both form chlorides and bromides that hydrolyze slowly and are soluble in ethanol;
$MgCl_2(s) + 2H_2O(l) \rightleftharpoons Mg(OH)Cl(l) + H_3O^+(aq) + Cl^-(aq)$

The oxonium ions produced makes the resultant solution acidic.

***Resemblance between Beryllium and aluminium*:**

(1) *Both elements are passive to concentrated nitric acid*.

(2) *Both react with conc. alkalis (to form complex)and mineral acids .(amphoteric metals)*

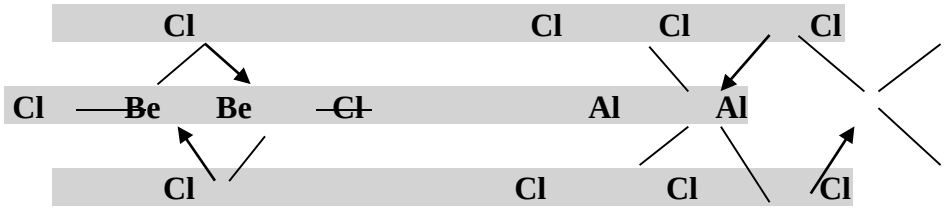
$Be(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Be(OH)_4^{2-}(aq) + H_2(g)$

$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2\ Al(OH)_4^-(aq) + 3H_2(g)$

$Be(s) + 2H^+(aq) \rightarrow Be^{2+}(aq) + H_2(g)$

$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

(3) *Both elements form chlorides which are partly covalent and exist as dimmers*.



(4) *Their oxides are amphoteric as are their hydroxides*.

Oxides

$BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow Be(OH)_4^{2-}(aq)$

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2\ Al(OH)_4^-(aq)$

$BeO(s) + 2H^+(aq) \rightarrow Be^{2+}(aq) + H_2(g)$

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$

Hydroxides

$Be(OH)_2(s) + 2OH^-(aq) \rightarrow Be(OH)_4^{2-}(aq)$

$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

$Be(OH)_2(s) + 2H^+(aq) \rightarrow Be^{2+}(aq) + 2H_2O(l)$

$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$

(5) Both their carbides hydrolyze in water to form methane gas.

$Be_2C(s) + 4H_2O(l) \rightarrow 2Be(OH)_2(s) + CH_4(g)$

$Al_4C_3(s) + 12H_2O(l) \rightarrow 4Al(OH)_3(s) + 3CH_4(g)$

Explanation as to why the two elements (Li & Mg, Be & Al, B & Si) show resemblance in chemical properties: *Similar* electro negativities, similar electrode potentials, similar hydration energies, similar ionization energies.

- their ions have similar charge densities and polarizing powers