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.

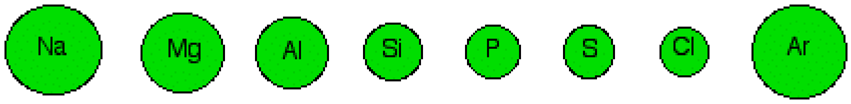
Explanation

- 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(1st 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.

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

$M^{+}_{(g)} \rightarrow M^{2+}_{(g)} + e^{-} \quad \triangle H=$ 2nd 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 1ST 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 1st 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 1st 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 1st 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 1st 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 1st ionization energy.

4. Electronic configuration of the outer most shell.

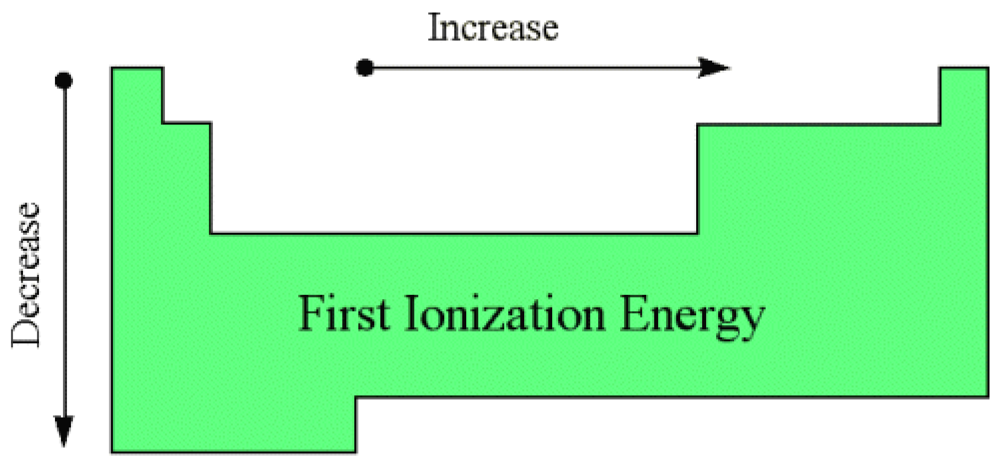
- ✓ When the first electron is coming from an outer sub-shell which is half full (eg. N: $1S^2 2S^2 2P^3$), a lot of energy is needed since the unpaired electrons experience minimum repulsion and the shell is thermodynamically stable.
- ✓ When the 1st electron is coming from an outer shell which is fully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

Within each group (column) the 1st 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.

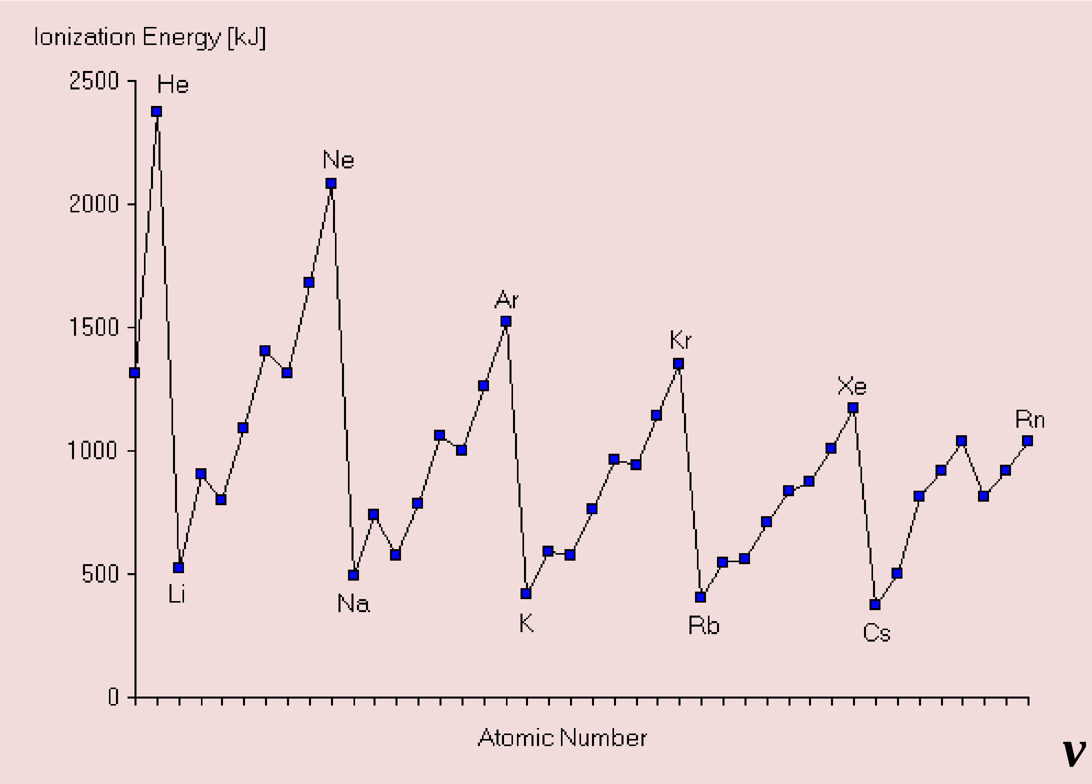
b) 1st ionization energy generally decreases down any group in the periodic Table.

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 outweighs 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 1st 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 (1st 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 1st 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 2nd short period from sodium to argon.

NB:

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

Helium : $1s^2$ has the highest 1st 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	1st I.E	2nd I.E	3rd I.E	4th 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 1st 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
1st I.E	1013	1000	1255	1519	418	590
2nd I.E	1904	2255	2297	2665	3067	1146
3rd 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 1st five ionization energies in K/J per mole for elements W-Z.

Element	1st	2nd	3rd	4th	5th
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:

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

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

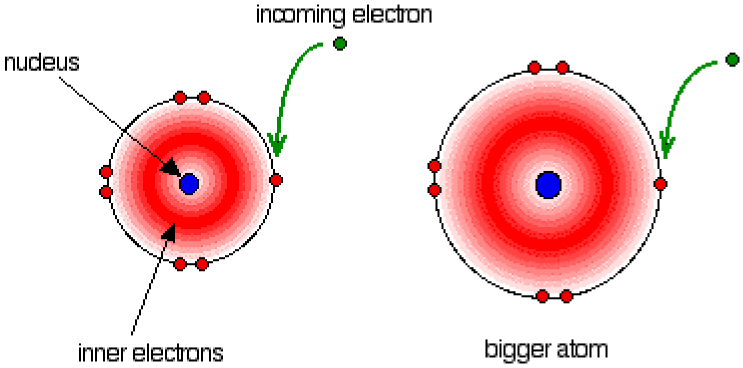
3. ELECTRON AFFINITY

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.

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

$X_{(g)} + e \rightarrow X^{-}_{(g)}$ $\triangle$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.

$X^{-}_{(g)} \quad + \quad e \quad \rightarrow \quad X^{2-}_{(g)} \qquad \triangle H = 2^{nd}$ 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 3rd ,4th ,5th 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.

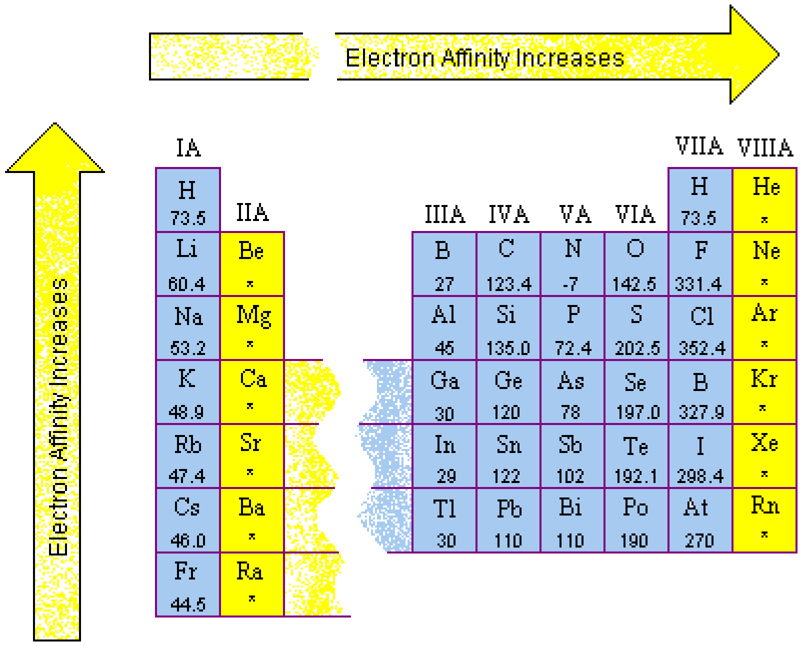
If the screening effect of the electrons in the inner shells is high, electron being added experiences a low attraction from the nucleus leading to a low value of electron affinity.

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



IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 73.5						H 73.5	He *
Li 60.4	Be *	B 27	C 123.4	N -7	O 142.5	F 331.4	Ne *
Na 53.2	Mg *	Al 45	Si 135.0	P 72.4	S 202.5	Cl 352.4	Ar *
K 48.9	Ca *	Ga 30	Ge 120	As 78	Se 197.0	B 327.9	Kr *
Rb 47.4	Sr *	In 29	Sn 122	Sb 102	Te 192.1	I 298.4	Xe *
Cs 46.0	Ba *	Tl 30	Pb 110	Bi 110	Po 190	At 270	Rn *
Fr 44.5	Ra *						

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 1st 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.

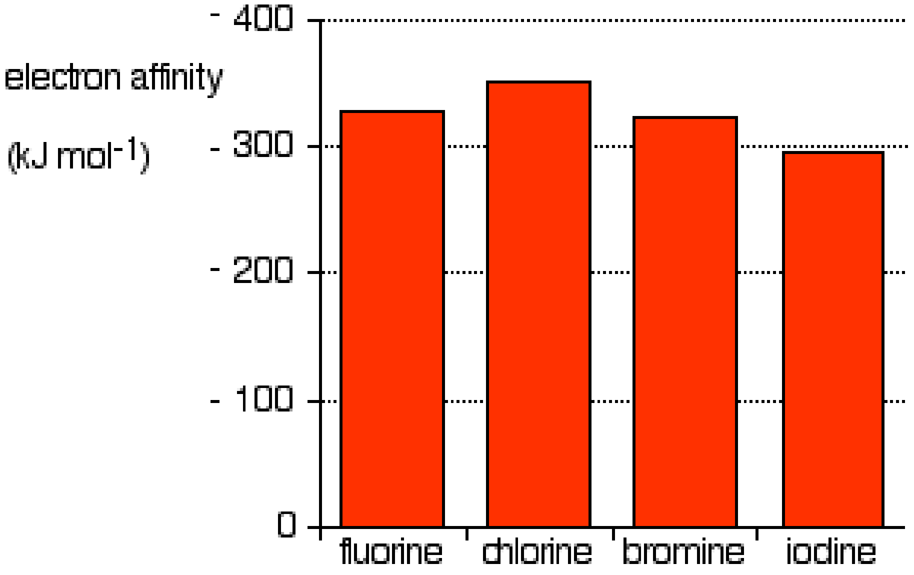
As the atomic radius increases down the group, the screening effect of the inner complete shells of electrons increases too.

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.

Electron affinity of the Group 7 elements



Electronegativity

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

$$\overset{\delta+}{H}-\overset{\delta-}{Cl}$$

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.

<u>Electronegativity:</u>

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 .

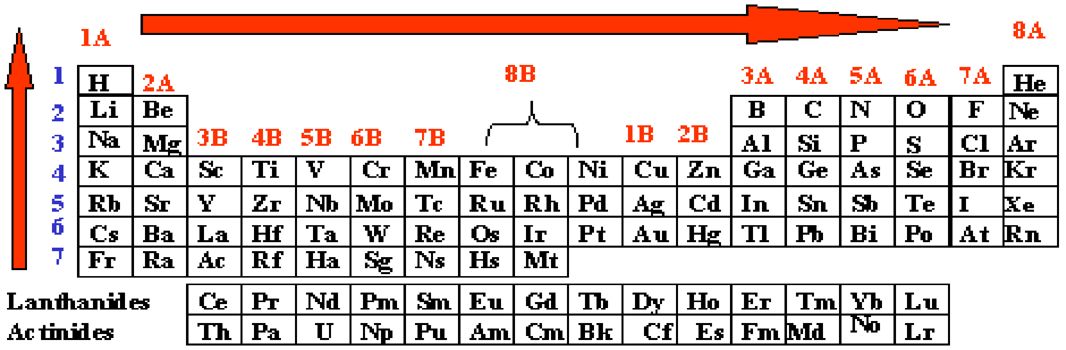
Group7

Element	Electro-negativity
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.

Electronegativity Trends in Periodic Table



Electronegativity increases from bottom to top in a column.
Electronegativity increases from left to right across a group.

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:

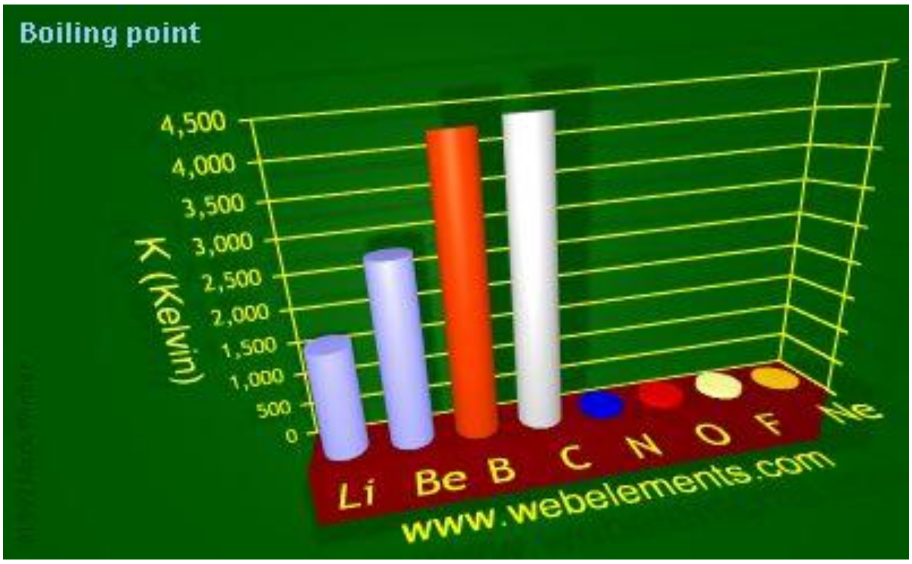
- Molecular mass
- Shape of molecules
- Type of intermolecular forces of attraction.

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.

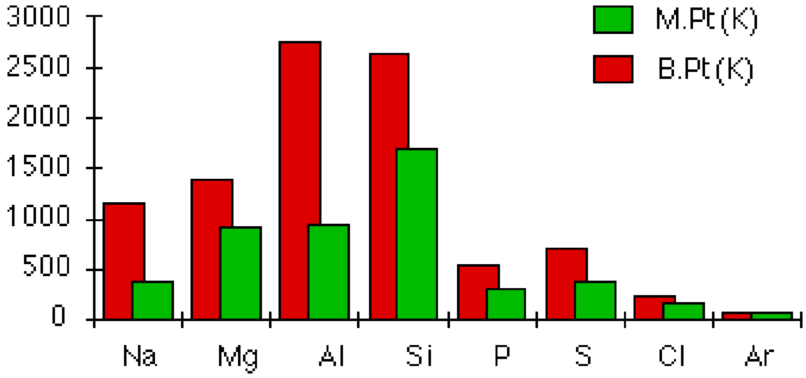
Li has a body centred cubic (b.c.c) structure which has its atoms less efficiently packed than Be with hexagonal closed packed (h.c.p).

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.

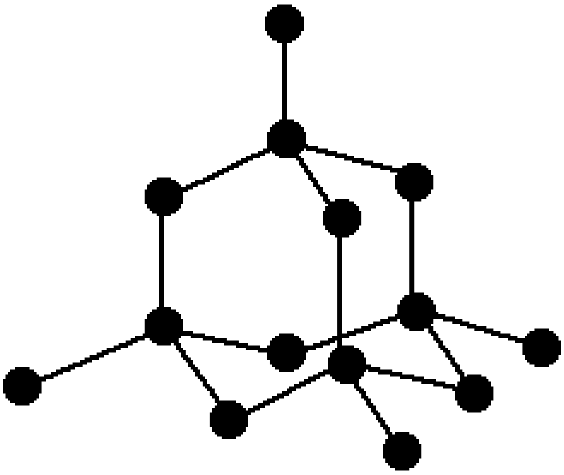
The number of electrons which each atom can contribute to the metallic bonding increases.

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.

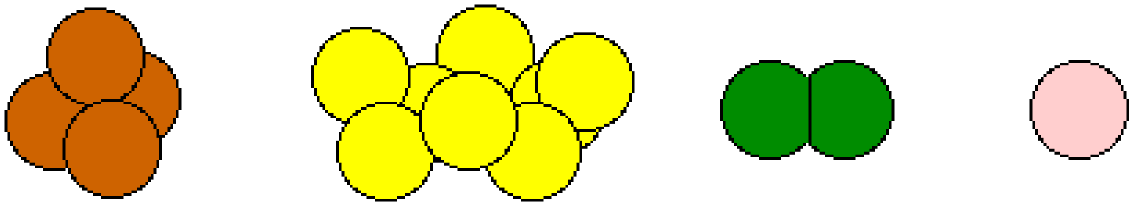
Silicon has the highest melting and boiling points because it has a giant covalent structure.

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.



a P_4 molecule

an S_8 molecule

a Cl_2 molecule

an Ar molecule

(not drawn to scale)

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.

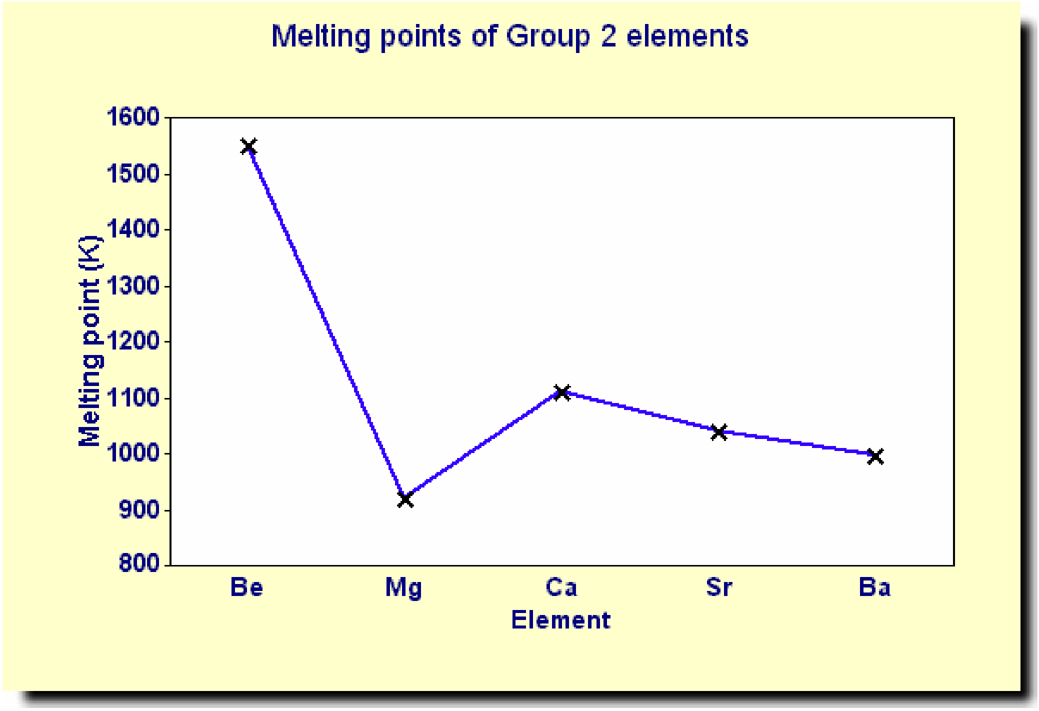
Chlorine

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.

$NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$ $\triangle$ H = 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.

$Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(s)}$ $\triangle$ H = 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.

$Na^{+}_{(g)} + aq \rightarrow Na^{+}_{(aq)}$ $\triangle$ H = 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.

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

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

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

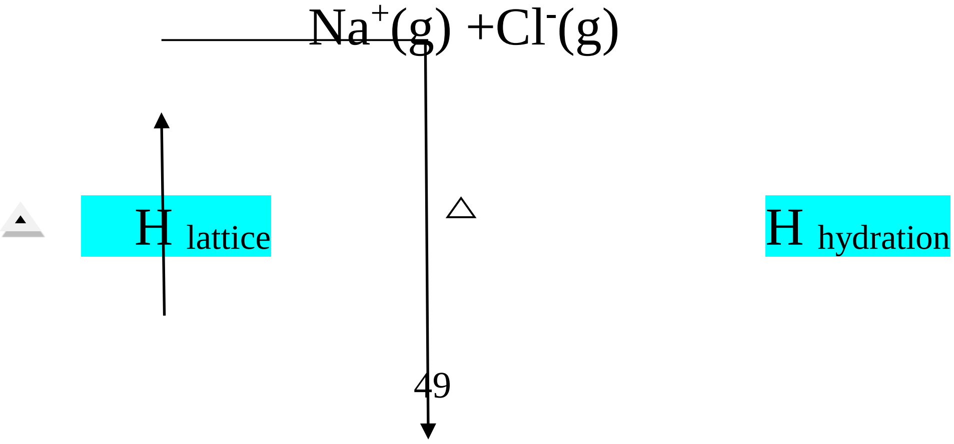
If the solvation energy is less than the lattice energy then the substance dissolves endothermically.

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

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

$$NaCl(s) + aq \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Δ H = Enthalpy of solution.



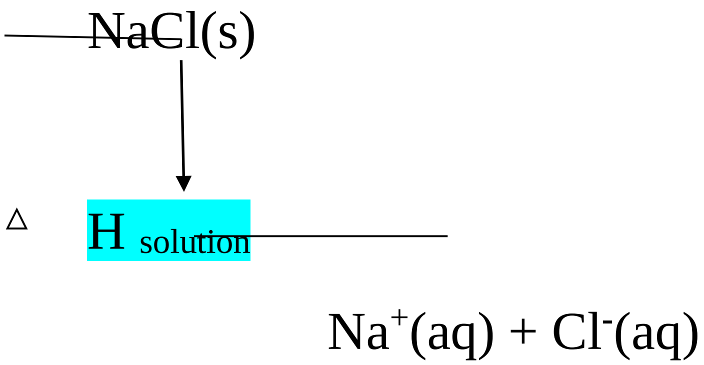


Figure shows Born-Haber cycle for solubility of NaCl.

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

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.

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

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

(4) both form carbonates that decompose on heating.

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

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

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

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

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

(6) Both form chlorides and bromides that hydrolyze slowly and are soluble in ethanol;

$MgCl_2(s) + 2H_2O(l) \qquad\qquad Mg(OH)Cl(l) + H_3O^+(aq) + Cl^-(aq)$

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)*

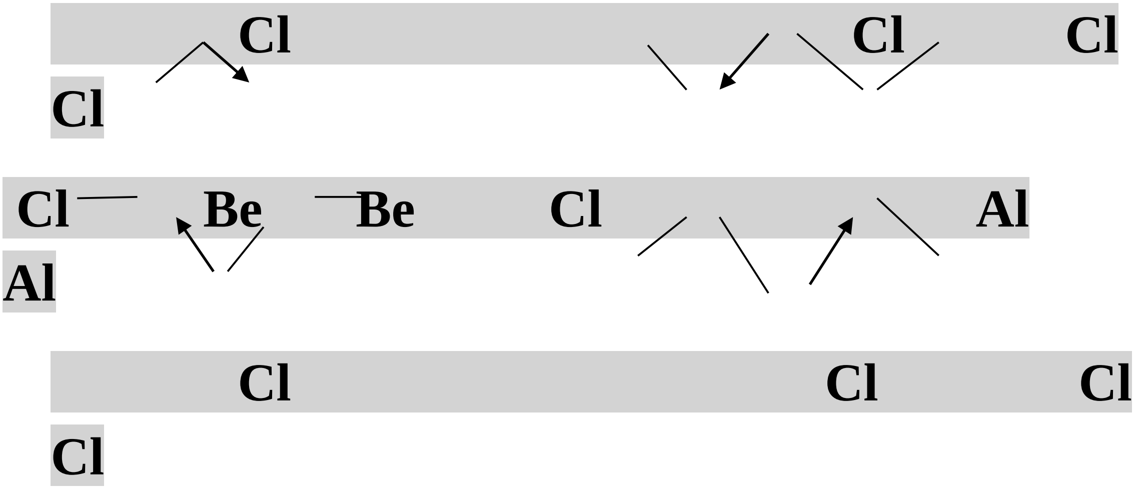
$Be(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Be(OH)_4^{2-}(aq) + H_2(g)$

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

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

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

(3) *Both elements form chlorides which are partly co-valent 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

GROUP 1 ELEMENTS(Alkali Metals)

(Li, Na, K, Rb, Cs)

The alkali metals are solids with body centred cubic (b.c.c) arrangement.

They have one valence electron with outer most shell electronic configuration of ns^1.

They have low melting and boiling point (only one electron available for bond formation).

They have the largest atomic radius and lowest ionization energy in any period.

They are highly electropositive and the most reactive metals.

GROUP 2 ELEMENTS(Alkaline Earth Metals)

(Be, Mg, Ca, Sr, Ba)

The alkaline earth metals are electropositive metals with 2 valence electrons (i.e. two electrons in their outer most shell).

The general electronic configuration of their outer shell is ns^2

They have a smaller atomic radii than corresponding group 1 metals.

They have higher melting and boiling points than corresponding group 1 metals.

They have a higher 1st ionization energies than corresponding elements in group 1.

They are less electropositive, less reactive and form more covalent compounds than group 1.

CHEMICAL PROPERTIES OF GROUP 1& 2 METALS

1. Reaction with Hydrogen.

The more electropositive metals of group 1 & 2 react with hydrogen to form ionic hydride except Be and Mg which form covalent hydride.

$2Na(s) + H_2(g) \rightarrow 2NaH(s)$

$Ca(s) + H_2(g) \rightarrow CaH_2(s)$

The ionic hydrides are hydrolyzed by water to form hydroxide and hydrogen gas.

$NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$

2. **Reaction with Water**.

All group 1 metals react with water more vigorously than their group II counterparts to form corresponding hydroxide and hydrogen gas. The vigor of reaction increases down the group.

Explanation

These metals form positive ions in the course of their reaction. Group I lose one electron while group II lose two electrons. Therefore less energy is required to remove one electron than two from the outer most shell as such group I metals react faster with water than corresponding metals of group II.

As the atomic radius increases down the group, ionization energy decreases thereby increasing reactivity in each group. *The lower the ionization energy, the lower the activation energy for reaction and thus the faster the reaction.*

- ✓ $2X(s) + H_2O(l) \rightarrow 2XOH(aq) + H_2(g)$. X = Li, Na, K, Rb, Cs.
- ✓ Be does not react with water.
- ✓ Magnesium has a very slight reaction with cold water, but burns in steam to form white MgO and hydrogen gas.

$$\mathbf{Mg(s) + H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g)}$$

(with cold water)

$$\mathbf{Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)}$$

. (with steam)

- ✓ Ca, Sr, and Ba react with increasing vigor with cold water to form corresponding hydroxide and hydrogen gas.

$$X(s) + 2H_2O(l) \rightarrow X(OH)_2(aq) + H_2(g)$$

X= Ca, Sr,& Ba.

NB

The hydroxides of Be & Mg have low solubility in water. However the solubility of hydroxides increase from $Ca(OH)_2$ through $Sr(OH)_2$ to $Ba(OH)_2$.

Explanation

Down the group, the radius of the cations increase while the charge on them remains the same. This leads to a decrease in both the lattice and hydration energies.

Therefore the increase in solubility of the hydroxides down the group is attributed to the fact that the lattice energy of the hydroxides decrease more rapidly than the hydration energy.

As such the lattice energy is easily superseded by the hydration energy thus facilitating solubility of the hydroxides.

See table below.

Hydroxide	Solubility per 100g of water at 25^0c
$Be(OH)_2$	0.00
$Mg(OH)_2$	0.01
$Ca(OH)_2$	0.15
$Sr(OH)_2$	0.89
$Ba(OH)_2$	3.32

3. **Reaction with Acid**.

i) *Dilute and concentrated hydrochloric acid*

They react similarly with group 2 metals to form corresponding salt and liberating hydrogen gas.

$M(s) + 2H^+(aq) \rightarrow M^{2+}(aq) + H_2(g)$ M= Be, Mg, Ca, Sr, Ba.

ii)*Dilute sulphuric acid*.

Be reacts with hot dilute sulphuric acid to form salt and hydrogen gas.

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

Mg reacts with cold dilute to form salt and hydrogen gas.

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

Ca, Sr & Ba react to form a sparingly soluble sulphate which renders the reaction passive.

iii) *Conc. sulphuric acid*

Be reacts in the same way as with dilute sulphuric acid.

However other members of the group react with conc. sulphuric acid to form salt, sulphur dioxide and water.

$M(s) + 2H_2SO_4(l) \rightarrow MSO_4(aq) + SO_2(g) + 2H_2O(l)$ M = Mg, Ca, Sr, Ba.

iv) *Nitric acid*.

Be does not react with nitric acid at all conditions.

Mg reacts with dilute nitric acid to form salt and hydrogen gas.

$Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$

Mg reacts with conc. nitric acid to form salt, nitrogen dioxide and water.

$Mg(s) + 4HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

Ca, Sr & Ba react with nitric acid to form salt, nitrogen dioxide and water.

$Ba(s) + 4HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

4. **Reaction with Oxygen**.

The s-block elements react with oxygen to form 3 types of oxides namely

- ❖Normal oxide (O^{2-})
- ❖Peroxide (O_2^{2-})
- ❖Superoxide (O_2^{-})

All group 1 metals form normal oxide with oxygen.

$4X(s) + O_2(g) \rightarrow 2X_2O(s)$ X= Li, Na, K, Rb, Cs.

Elements Na to Cs in addition form peroxides of the type X_2O_2

$2X(s) + O_2(g) \rightarrow X_2O_2(s)$ X= Na, K, Rb, Cs.

Elements K to Cs in addition form superoxide.

$X(s) + O_2(g) \rightarrow XO_2(s)$ X= K, Rb ,Cs

NB:

Li can not form higher oxides due to the fact that Li^+ is very small, with high charge density & high polarizing power. Thus the larger oxides can not be accommodated around it otherwise the compound would be highly covalent & unstable.

All group 2 metals when heated form normal oxide in oxygen.

$2M(s) + O_2(g) \rightarrow 2MO(s)$ M= Be, Mg, Ca, Sr, Ba

The more electropositive metals form peroxides e.g Sr & Ba.

$M(s) + O_2(g) \rightarrow MO_2(s)$ M = Sr, Ba

NB:

The tendency to form peroxide increases down the group. This is because the radii of the cations increase down the group, as such their charge densities and polarizing powers decrease. Therefore the larger peroxide can easily be accommodated around the cation with least polarization forming stable lattice.

Beryllium oxide is amphoteric, shows both basic and acidic properties.

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

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

The other oxides are ionic and basic in nature.

(5) **Reaction with halogens**.

All the metals of group 1 & 2 combine directly under heat to form chlorides.

$2Li(s) + Cl_2(g) \rightarrow 2LiCl(s)$

$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$

COMPOUNDS OF GROUP 1 & 2

1) Compounds of group(ii) tend to be less ionic than those of group(i).

Explanation:

- ✓ The cations of group 2 have smaller ionic radius than corresponding group 1.
- ✓ Group 2 cations are doubly charged while those of group 1 are singly charged.

- ✓ Therefore cations of group 2 have higher charge density and more polarizing power than corresponding group 1. As such compounds of group 2 are less ionic than corresponding group1 compounds. e.g. $MgCl_2$ and NaCl.

2) Salts of group 2 elements are less soluble in water than the corresponding group 1 salts.

Explanation

- ➢ The cations of group 2 have smaller ionic radius than corresponding group 1.
- ➢ Group 2 cations are doubly charged while those of group 1 are singly charged.
- ➢ Therefore the lattice energy of group 2 salts are much higher than those of corresponding group 1 salts.

The higher lattice energy of group 2 salts make them less soluble than their corresponding group 1 salts.

SULPHATES OF GROUP 1 & 2

Sulphates of group 1 are white solids which are stable to heat and are readily soluble in water.

Sulphates of group 2 are white solids and sparingly soluble in water. Their solubility decrease down the group.

Sulphate	Solubility per 100g of water at 25^0c
$BeSO_4$	43
$MgSO_4$	36
$CaSO_4$	0.20
$SrSO_4$	0.011
$BaSO_4$	0.0024

Explanation.

Down the group, the radius of the cations increase while the charge on them remains the same. This leads to a decrease in both the lattice and hydration energies.

Therefore the decrease in solubility of the sulphates down the group is attributed to the fact that the hydration energy of the suphates decreases more rapidly than the lattice energy down the group.

NB

Solubility of the nitrates , carbonates and chromates are similar to those of the sulphates.

CARBONATES OF GROUP 1 & 2

The carbonates of group1 metals are white solids ,readily dissolve in water and are stable to heat except lithium carbonate which decomposes on heating.

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

Explanation

Li^+ ion has a very small radius giving it a high charged density and a high polarizing power. As such the smaller oxide ion (O^{2-}) with a similar charged density approaches the Li^+ ion with least polarization thus forming a stable oxide.

However, as the group is descended the radii of the cations increase and their charged densities decrease. Thus they can not easily be accommodated around the smaller oxide ion due to its high polarizing effect.

Carbonates of group 2 decompose on heating to form the metal oxide and carbondioxide gas.

$XCO_3(s) \rightarrow XO(s) + CO_2(g)$ X= Be, Mg, Ca, Sr, Ba.

The thermal stability of the carbonates increases as the group is descended.

Carbonate	Decomposition temp. ^0C
$BeCO_3$	100
$MgCO_3$	350
$CaCO_3$	900
$SrCO_3$	1290
$BaCO_3$	1350

Explanation

On descending the group, the charged densities of the metal cations progressively decrease due to increase in cationic radius.

Since an oxide is smaller than a carbonate, the decomposition of metal carbonates become less energetically favourable down the group.

NITRATES OF GROUP 1 & 2

Group 1 nitrates (except lithium nitrate) decompose to form nitrites and oxygen.

$2XNO_3(s) \rightarrow 2XNO_2(s) + O_2(g)$ X= Na, K, Rb, Cs.

However lithium nitrate decomposes to form metal oxide, nitrogen dioxide and oxygen.

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

Explanation

The oxide(O^{2-})ion is much smaller than the NO_3^- ion. Li^+ ion has a very small radius giving it a high charge density and a high polarizing power.

As such the smaller oxide ion (O^{2-}) with a similar charged density approaches the Li^+ ion more closely with least polarization thus forming a stable oxide.

However, as the group is descended the radii of the cations increase and their charge densities decrease. Their nitrates decompose to a relatively smaller nitrites. The decrease from nitrate to nitrite stabilizes the compound.

COMPLEX FORMATION BY GROUP 2 CATIONS

Complex ion formation is favoured by:

- Presence of empty orbitals on the cations to accommodate the lone pairs of electrons donated by ligands.
- Small radius of cation.
- High charge on the cation.

E.g $Be(OH)_4^-$, $Be(H_2O)_4^{2+}$

Beryllium cation forms complex easily due to its very small ionic radius & high charge density.

The tendency to form complex ions decreases rapidly down the group with increasing cationic radius & decrease in the charge density of cations. This is because the attraction for the lone pairs of electrons on the ligands decrease.

Reactions in which Be resembles other group 2 elements include:

- All burn in air to form normal oxide.
- All react with chlorine gas when heated to form chloride.
- All react with dilute hydrochloric acid liberating hydrogen gas.

Reactions in which Be differs from other group 2 metals include:

- Be reacts with conc. alkalis but others don't.
- BeO oxide is amphoteric, reacts with both acid and alkalis. Other oxides of the group are basic in nature.
- Be carbide reacts with water to form methane. Other members of the group don't.
- Be forms chloride which is partly covalent and exist as dimmers. Other members form ionic chlorides.

- Be forms only one type of oxide, the monoxide . Other members form more than one type of oxide.

Qn.

A chloride of beryllium Z, contains 11.25% beryllium and 88.75% of chlorine.

i) Calculate the empirical formula of Z.

ii) Determine the molecular formula of Z(vapor density of Z=80).

iii) Write the structural formula of Z.

Qn.

A chloride of aluminium X, contains 20% aluminium and 80% chlorine.

i) Calculate the empirical formula of X.

ii) Determine the molecular formula of X(vapor density of X= 133.5).

iii) Write the structural formula of X.

Qn.

When 0.13g of a chloride of iron was vaporized at 600k and 1 atmosphere pressure, 20cm^3 of vapor was formed.

i) Calculate the relative mass of iron chloride.

ii) Determine the molecular formula of the iron chloride.

iii) Write the structural formula of the iron chloride.

Qn.

i) Compare the reaction of beryllium and barium with sulphuric acid under various conditions.

ii) Explain how the solubility and basicity of the hydroxides of the elements of group 2 in the Periodic Table vary down the group.

Qn.

Describe the reactions, if any, between each of the following elements, Be, Mg and Ca with:

i) warm dilute sulphuric acid.

ii) warm conc. sodium hydroxide.

4. ALUMINIUM

Ore of aluminium is called Bauxite, $Al_2O_3.xH_2O$

Impurities found in the ore are:

- Silica, SiO_2

- iron(iii) oxide,Fe_2O_3

In order to obtain pure aluminium, the ore must first be refined to eliminate the impurities stated above.

Purification of bauxite

The ore is roasted and then crushed to powder.

Conc. sodium hydroxide is added to dissolve the amphoteric oxide, Al_2O_3 and the acidic oxide SiO_2

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

$$\mathbf{SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)}$$

The impurity, Fe_2O_3 , is eliminated by filtering off.

Aluminium is then re-precipitated as $Al(OH)_3.xH_2O$ by either:

i) by adding a little prepared aluminium hydroxide to the filtrate.

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

ii) by bubbling CO_2 gas through the filtrate to remove the excess OH^- ions.

$$\mathbf{2Al(OH)_4^-{}_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO_3^{2-}{}_{(aq)}}$$

The hydroxide, $Al(OH)_3$ is heated to form aluminium (III)oxide.

$$2Al(OH)_3 \rightarrow Al_2O_3(s) + 3H_2O(g)$$

Extraction of Aluminium (By electrolysis of the fused ore)

The pure oxide is 1st dissolved in molten cryolite (sodium aluminium fluoride - Na_3AlF_6) to lower its melting point.

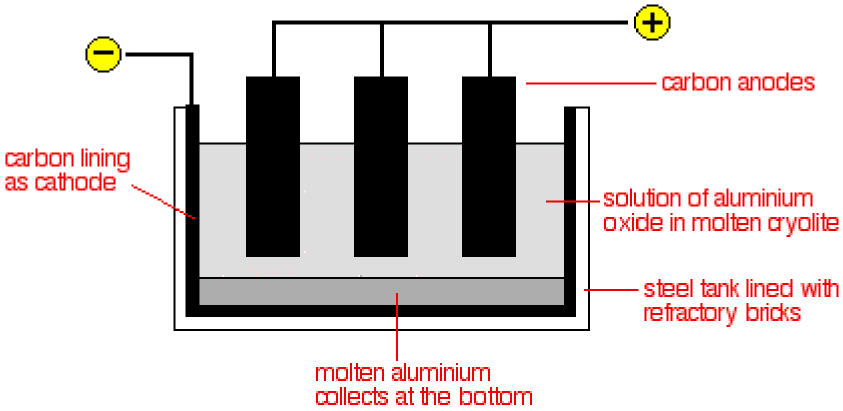
The melt is then electrolyzed at a temperature between 800-900 ^{0}c at a high current density between graphite electrodes.

Molten aluminium sinks to the bottom at the cathode where it is tapped off while oxygen is liberated at the carbon anode.

Cathode: $Al^{3+}_{(l)} + 3e^- \rightarrow Al_{(l)}$

Anode: $2O^{2-}_{(l)} \rightarrow O_{2(g)} + 4e^-$

The electrolysis cell



Reactions of aluminium

a) **Reaction with water**.

Aluminium reacts slowly with steam to form the oxide and hydrogen gas.

$$2Al(s) + 3H_2O(g) \rightarrow Al_2O_3(s) + 3H_2(g)$$

b) **Reaction with chlorine**.

Aluminium when heated reacts with dry chlorine to form a chloride which sublimes. The chloride is predominantly covalent.

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

Explanation

Aluminium forms a smaller cation with high charge density & high polarizing power. It distorts the electron cloud of surrounding anions. The larger the anion, the greater the extent of polarization. Therefore the large chloride ion is polarized greatly and as such a covalent character is induced.

The chloride forms dimer , Al_2Cl_6 , at high temperature with a chloride bridge structure. Aluminium bromide & iodide have similar structures.

c) **Reaction with solution of alkalis (NaOH & KOH).**

Aluminium is an amphoteric metal. It reacts with concentrated alkalis to form aluminates complex and hydrogen gas.

$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \rightarrow 2\ Al(OH)_4^-{}_{(aq)} + 3H_{2(g)}$

d) **Reaction with acids**.

With dilute mineral acids except nitric acid, aluminium forms salt and hydrogen gas.

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

With hot conc. H_2SO_4, aluminium forms salt, sulphurdioxide gas and water.

$2Al(s) + 6H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3SO_2(g) + 6H_2O(l)$.

Aluminium does not react with dilute nitric acid . The metal is rendered passive due to the formation of an impervious layer of oxide.

The acidity of the hexa-aqua ions

In aqueous solution, soluble salts of aluminium i.e. $AlCl_3$, $Al_2(SO_4)_3$ etc exist as $[Al(H_2O)_6]^{3+}$.

The resultant solution is acidic due to hydrolysis reactions:

$$\mathbf{[Al(H_2O)_6]^{3+}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [Al(H_2O)_5OH]^{2+}{}_{(aq)} + H_3O^+{}_{(aq)}}$$

$$\mathbf{[Al(H_2O)_5OH]^{2+}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [Al(H_2O)_4 2OH]^{+}{}_{(aq)} + H_3O^+{}_{(aq)}}$$

$$\mathbf{[Al(H_2O)_4 2OH]^{+}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [Al(H_2O)_3 3OH]_{(s)} + H_3O^+{}_{(aq)}}$$

Over all equation:

$$\mathbf{[Al(H_2O)_6]^{3+}{}_{(aq)} + 3H_2O_{(l)} \leftrightarrow [Al(H_2O)_3 3OH]_{(s)} + 3H_3O^+{}_{(aq)}}$$

white ppt

The hydroxonium ions produced make the resultant solution acidic with PH less than 7 and a white solid is formed.

If sodium carbonate solution is bubbled through aqueous solution of aluminium salts, bubbles of a colorless gas that turns lime water milky is formed.

The oxide and hydroxide of aluminium are amphoteric. They react with both conc. alkalis and dilute acids.

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

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

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

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

Some uses of aluminium include:

Aluminium is used for:	**Because**
1. Aircraft	light, strong, resists corrosion

2. other transport such as ships' superstructures, container vehicle bodies, tube trains	light, strong, resists corrosion
3. overhead power cables .	light, resists corrosion, good conductor of electricity
4. Saucepans	light, resists corrosion, good appearance, good conductor of heat

5. GROUP (IV) ELEMENTS

(Carbon, Silicon, Germanium, Tin, and Lead)

- ✓ All group(iv) elements have four electrons in their outermost shell with a general outer configuration of ns^2np^2

  n=2 for C, n=3 for Si, n=4 for Ge, n=5 for Sn n=6 for Pb etc

- ✓ Metallic character increases down the group as the radius of the atoms become larger. Carbon and Silicon are non metals , Germanium is a metalloid ie it exhibits properties characteristics of metals and non metals. While Tin & Lead are weak metals.eg they form amphoteric oxides
- ✓ All elements show an oxidation states of +2 and +4. The +2 oxidation state arise due to the inability of the outer most paired ‘s’ electrons to take part in bond formation. This is called the inert pair effect.
- ✓ The stability of the +2 oxidation state increases down the group from carbon to lead. This is due to increasing metallic character and increasing inert pair effect as the group is descended.eg Carbon and Silicon form extremely unstable compounds in +2 oxidation state.

- ✓ Germanium and tin compounds in +2 oxidation state are predominantly covalent and are readily oxidized ie they are powerful reducing agent.
- ✓ Lead invariably forms more stable compounds in +2 oxidation state than +4 oxidation state. Also compounds of lead in +2 oxidation state are ionic in nature. Therefore lead (iv) compounds are unstable, and readily decompose to +2 oxidation state.eg

  $$2\,\mathbf{PbO_{2(s)}} \rightarrow \mathbf{2PbO_{(s)}} + \mathbf{O_{2(g)}}$$

  $$\mathbf{PbCl_{4(l)}} \rightarrow \mathbf{PbCl_{2(s)}} + \mathbf{Cl_{2(g)}}$$

- ✓ The stability of +4 oxidation state decreases down the group. Carbon , silicon and germanium form more stable compounds in +4 oxidation state than in +2. This could explain why their compounds in +2 oxidation states are good reducing agents.
- ✓ Carbon is the only member of the group whose covalency is restricted to a maximum of +4.This is due to absence of the vacant ‘d’ orbitals. Other elements have a maximum of +6 due to the availability of vacant d-orbitals which allows them to expand their octet.
  - ✓ Hoverer, all the elements exhibit a covalency of 4 but compounds of the type M^{4+} or M^{4-} are rare.

This is because the sum of the first four ionization energies or first four electron affinities would be highly endothermic. An ion of the type M^{4+} would be very small with high charged density as such would exert high polarizing effect on the surrounding anion thus making the compound formed highly covalent & unstable.

NB:

Carbon, however, being the most electronegative with the smallest atomic radius and least number of electrons is most likely to form compounds of the type M^{4+} or M^{4-}

- ✓ Carbon exhibit a unique property of catenation. This is the ability of an element to form covalent bonds with its own atoms so as to produce long chains and rings.
- ✓ Carbon therefore form limitless hydrides, alkanes, alkenes, alkynes etc due to catenation. This unique property of carbon is attributed to the small atomic radius of carbon. The electrons involved in bond formation between two carbon atoms are closer to the nuclei and are strongly

held by it thus making bonds very strong and stable. However as you descend the group, atomic radius increases. Therefore electrons between the atoms become more distant from the nuclei making the bond weaker and unstable.

- ✓ The melting points of group(iv) elements decrease as the group is descended. Carbon, however, has a much higher melting point than others. This is because carbon has a giant molecular (Macro-molecular) structure composed of many atoms due to its ability to catenate. It has abnormally high melting point because large number of short and strong carbon –carbon bonds have to be broken before it melts.

Melting point then decreases gradually from silicon to lead in line with increase in atomic radius down the group. The inter-atomic bond length (element-element bonds) become longer and weaker thus melting point decreases.

CHEMICAL PROPERTIES OF GROUP (IV) ELEMENTS.

1.Reaction with water.

Carbon reacts with steam when heated to form carbon monoxide and hydrogen gas.

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

Silicon reacts with steam when heated to form silicon dioxide and hydrogen gas.

$$Si_{(s)} + 2H_2O_{(g)} \rightarrow SiO_{2(s)} + 2H_{2(g)}$$

Germanium and Tin do not react with water at any condition.

Lead reacts slowly with soft water forming lead(ii) hydroxide.

$$2Pb_{(s)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 2Pb(OH)_{2(s)}$$

NB

The above reaction leads to lead poisoning and explains why lead pipes are not used for transporting water for drinking.

2. Reaction with Oxygen (air).

a) Carbon.

When carbon is heated in limited air, carbon monoxide is formed and in excess air, carbondioxide is formed.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

$C(s) + O_2(g) \rightarrow CO_2(g)$

b) When the rest of the elements are heated with oxygen , they form dioxides except lead which forms lead(ii) oxide.

$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)}$
$Ge_{(s)} + O_{2(g)} \rightarrow GeO_{2(s)}$
$Sn_{(s)} + O_{2(g)} \rightarrow SnO_{2(s)}$
$2Pb_{(s)} + O_{2(g)} \rightarrow 2PbO_{(s)}$

3. Reaction with acids.

a) Carbon is attacked by all oxidizing acids eg hot conc. Sulphuric acid and hot conc. Nitric acids.

$C_{(s)} + 4HNO_{3(aq)} \rightarrow CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$
$C_{(s)} + 2H_2SO_{4(aq)} \rightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$

b) Silicon is resistant to all acids except hydrofluoric acid (HF)

$Si_{(s)} + 6HF_{(aq)} \rightarrow H_2SiF_{6(aq)} + 2H_{2(g)}$

c) Germanium, Tin and Lead are oxidized by hot conc. nitric acid

$3Ge_{(s)} + 4HNO_{3(aq)} \rightarrow 3GeO_{2(s)} + 2H_2O_{(l)} + 4NO_{(g)}$
$3Sn_{(s)} + 4HNO_{3(aq)} \rightarrow 3SnO_{2(s)} + 2H_2O_{(l)} + 4NO_{(g)}$

$Pb_{(s)}$ +$4HNO_{3(aq)}$ → $Pb(NO_3)_{2(aq)}$ + $2H_2O_{(l)}$ + $2NO_{2(g)}$

Lead is rendered passive in both cold dilute hydrochloric and sulphuric acids due to formation of insoluble salt of lead(ii) chloride & lead(ii) sulphate respectively.

However, lead reacts with hot dilute hydrochloric acid to form lead(ii) chloride and hydrogen gas.

$Pb_{(s)}$ + $2HCl_{(aq)}$ → $PbCl_{2(aq)}$ + $H_{2(g)}$

Tin reacts with hot conc. Sulphuric acid to form tin(iv) sulphate.

$Sn_{(s)}$ + $4H_2SO_{4(aq)}$ → $Sn(SO_4)_{2(aq)}$ + $2SO_{2(g)}$ + $4H_2O_{(l)}$

Lead reacts with hot conc. Sulphuric acid to form lead(ii) sulphate, sulphur dioxide and water.

$Pb_{(s)}$ + $2H_2SO_{4(aq)}$ → $PbSO_{4(s)}$ + $SO_{2(g)}$ + $2H_2O_{(l)}$

This reaction is similar to Al & Chromium

4. Reaction with Alkalis

Carbon is resistant to alkalis but silicon dissolves in conc. Solution to form silicate.

$Si_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2SiO_{3(aq)} + 2H_{2(g)}$

$(2KOH_{(aq)})$

Germanium dissolves in conc. Alkalis to form hexa-hydroxo-germanate (iv)

$Ge_{(s)} + 2KOH_{(aq)} + 4H_2O_{(l)} \rightarrow K_2Ge(OH)_{6(aq)} + 2H_{2(g)}$

Ionically:

$Ge_{(s)} + 2\,OH^-_{(aq)} + 4H_2O_{(l)} \rightarrow Ge(OH)_6{}^{2-}{}_{(aq)} + 2H_{2(g)}$

Tin and Lead dissolve slowly in hot conc. Solution of alkalis to form hexahydroxystannate(ii) and plumbate(ii) respectively.

$Sn_{(s)} + 4KOH_{(aq)} + 2H_2O_{(l)} \rightarrow K_4Sn(OH)_{6(aq)} + H_{2(g)}$

$Pb_{(s)} + 4KOH_{(aq)} + 2H_2O_{(l)} \rightarrow K_4Pb(OH)_{6(aq)} + H_{2(g)}$

COMPOUNDS OF GROUP(IV) ELEMENTS

Group(iv) elements form compounds in +2 and +4 oxidation states. The +2 oxidation state becomes more stable while the stability of +4 decreases as the group is descended.

THE OXIDES OF GROUP 4

These elements form oxides of the type XO, wherein the element shows an oxidation state of +2 and also of the type XO_2, wherein the element shows an oxidation state of +4.

The oxides of the elements at the top of Group 4 are acidic, but acidity of the oxides falls as you go down the Group. Towards the bottom of the Group, the oxides become more basic - although without ever losing their acidic character completely.

The trend is therefore from acidic oxides at the top of the Group towards amphoteric ones at the bottom.

An oxide which can show both acidic and basic properties is said to be amphoteric.

MONOXIDES

The monoxide of carbon and silicon are usually treated as neutral oxides, but in fact carbon monoxide is very, very slightly acidic. It doesn't react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.

$$NaOH + CO \longrightarrow HCOONa$$

The fact that the carbon monoxide reacts with the basic hydroxide ion shows that it must be acidic

Those of germanium, tin and lead are amphoteric. The amphoteric monoxides (GeO, SnO and PbO) react with acids to give corresponding salts and alkalis to give germanate(ii), stannate(ii) and plumbate(ii) complex ions.

$SnO_{(s)} + 2H^{+}_{(aq)} \rightarrow Sn^{2+}_{(aq)} + H_2O_{(l)}$

$SnO_{(s)} + 2OH^{-}_{(aq)} + H_2O_{(l)} \rightarrow Sn(OH)_4^{2-}{}_{(aq)}$

Similar reactions are undergone by GeO & PbO

Alternatively:

$XO_{(s)} + 2OH^{-}_{(aq)} \rightarrow XO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

$GeO_{(s)} + 2OH^{-}_{(aq)} \rightarrow GeO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

$SnO_{(s)} + 2OH^{-}_{(aq)} \rightarrow SnO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

$PbO_{(s)} + 2OH^{-}_{(aq)} \rightarrow PbO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

They all react with concentrated hydrochloric acid.

$$XO_{(s)} + 2HCl_{(aq)} \longrightarrow XCl_{2(aq)} + H_2O_{(l)}$$

. . . where X can be Ge and Sn, but unfortunately needs modifying a bit for lead.

Lead(II) chloride is fairly insoluble salt in water and, , it would form an insoluble layer over the lead(II) oxide if dilute hydrochloric acid is used - stopping the reaction from going on.

$$PbO_{(s)} + 2HCl_{(aq)} \longrightarrow PbCl_{2(s)} + H_2O_{(l)}$$

However, using concentrated hydrochloric acid the large excess

of chloride ions in the concentrated acid react with the lead(II) chloride to produce a yellow soluble complex $PbCl_4^{2-}$.

$$PbCl_{2(s)} + 2Cl^-_{(aq)} \longrightarrow PbCl_4^{2-}{}_{(aq)}$$

DIOXIDES

The first four dioxide are prepared by heating the elements in oxygen but a similar process with lead gives lead(ii) oxide.

$$C_{(s)} \quad + \quad O_{2(g)} \quad \rightarrow \quad CO_{2(g)}$$

$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)}$
$Ge_{(s)} + O_{2(g)} \rightarrow GeO_{2(s)}$
$Sn_{(s)} + O_{2(g)} \rightarrow SnO_{2(s)}$
$2\,Pb_{(s)} + O_{2(g)} \rightarrow 2PbO_{(s)}$
NB

Lead(iv) oxide is made by action of hot dilute nitric acid on red lead, Pb_3O_4.

$Pb_3O_{4(s)} + 4HNO_{3(aq)} \rightarrow PbO_{2(s)} + 2Pb(NO_3)_{2(aq)} + 2H_2O_{(l)}$

Brown solid

With warm conc. HCl, red lead reacts according to the equation:

$Pb_3O_{4(s)} + 14HCl_{(aq)} \rightarrow 3H_2PbCl_{4(aq)} + Cl_{2(g)} + 4H_2O_{(l)}$

Yellow solution

Red lead is used in paints to prevent the corrosion of iron

In the case of lead(IV) oxide, the reaction has to be done with ice-cold hydrochloric acid. If the reaction is done any warmer, the lead(IV) chloride decomposes to give lead(II) chloride and chlorine gas. This is an effect of the preferred oxidation state of lead being +2 rather than +4.

Here the acid should be cold and conc.

$$\mathbf{PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{4(l)} + 2\,H_2O_{(l)}}$$

If the reaction is carried out at elevated temperature, lead(iv) oxide oxidizes hot conc. hydrochloric acid to chlorine gas.

$\mathbf{PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{2(aq)} + 2\ H_2O_{(l)} + Cl_{2(g}}$

The acidic nature of the dioxides

The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form $[X(OH)_6]^{2-}$.

$GeO_{2(s)} + 2OH^-_{(aq)} \rightarrow GeO_3^{2-}{}_{(aq)} + H_2O_{(l)}$

$SnO_{2(s)} + 2OH^-_{(aq)} \rightarrow SnO_3^{2-}{}_{(aq)} + H_2O_{(l)}$

$PbO_{2(s)} + 2OH^-_{(aq)} \rightarrow PbO_3^{2-}{}_{(aq)} + H_2O_{(l)}$

THE HALIDES OF GROUP 4

+2 halides

Carbon and Silicon do not form +2 halides. Those of Ge, Sn and Pb can be prepared by heating the tetra-chlorides with the free metal.

$GeCl_{4(l)} + Ge_{(s)} \rightarrow 2GeCl_{2(s)}$

$SnCl_{4(l)} + Sn_{(s)} \rightarrow 2SnCl_{2(s)}$

$PbCl_{4(l)} + Pb_{(s)} \rightarrow 2PbCl_{2(s)}$

Tin(ii) chloride may be prepared in anhydrous form by passing dry HCl gas over heated tin.

$Sn_{(s)} + 2HCl_{(g)} \rightarrow SnCl_{2(s)} + H_{2(g)}$

Lead(ii) chloride can also be prepared either by action of hot conc. HCl over lead(iv) oxide or by passing dry hydrogen chloride gas or chlorine over heated metal.

$PbO_2(s) + 4HCl_{(aq)} \rightarrow PbCl_2(s) + 2H_2O(l) + Cl_2(g)$

Conditions: hot/ conc. acid,

NB: Lead(ii) chloride is more soluble in concentrated hydrochloric acid than in water. Explain this observation.

Lead(ii) chloride has a high lattice energy which is not over-come on addition of cold water. However on heating, the high lattice energy is overcome and therefore lead(ii) chloride dissolves in hot water.

Lead(ii) chloride dissolves in conc. Hydrochloric acid due to formation of a soluble complex tetra- chloroplumbate(ii) ions.

$PbCl_{2(s)} + 2Cl^{-}_{(aq)} \rightarrow PbCl_4^{2-}{}_{(aq)}$

Yellow solution.

+4 halides

All the elements form tetra chlorides of the type XCl_4, which are covalently bonded and are volatile liquids.

All the tetra chlorides have a tetrahedral shape in which the element is surrounded by 4 chlorine atoms.

Preparation of the tetra chlorides

CCl_4

By reacting chlorine with carbon disulphide .

$CS_{2(l)} + 3Cl_{2(g)} \xrightarrow{AlCl_3/heat} CCl_{4(l)} + S_2Cl_{2(l)}$

The two liquids are separated by fractional distillation.

$SiCl_4$, $GeCl_4$ & $SnCl_4$

Are prepared by passing a stream of dry chlorine over the heated metal.

$Si_{(s)} + 2Cl_{2(g)} \rightarrow SiCl_{4(l)}$

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$Ge_{(s)} + 2Cl_{2(g)} \rightarrow GeCl_{4(l)}$

$Sn_{(s)} + 2Cl_{2(g)} \rightarrow SnCl_{4(l)}$

If a stream of chlorine is passed over heated lead, only lead(ii) chloride is formed.

$Pb_{(s)} + Cl_{2(g)} \rightarrow PbCl_{2(s)}$

To prepare lead(iv) chloride, use ice cold conc. HCl on lead(iv) oxide.

$PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{4(l)} + 2\ H_2O_{(l)}$

Hydrolytic behavior of the tetrachloride

CCl_4 does not under go hydrolysis in water. This is attributed to absence of the empty/ vacant d-orbitals.

However, other tetrachlorides under go hydrolysis in water. This is attributed to availability of the empty d-orbitals thereby allowing the elements to expand their octet and show a covalency of more than +4. This empty d-orbitals accept lone pairs of electrons from the oxygen atom of water molecule thus facilitating the hydrolysis of the tetra chlorides.

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$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$

White solid.

$GeCl_4(l) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(g)$

$SnCl_4(l) + 2H_2O(l) \rightarrow SnO_2(s) + 4HCl(g)$

$PbCl_4(l) + 2H_2O(l) \rightarrow PbO_2(s) + 4HCl(g)$

Brown solid

NB: In each case white fumes of hydrogen chloride gas is formed.

Stability of the tetrachloride

The tetrachlorides of carbon, silicon, and germanium are stable to heat, but those of tin and lead decompose on heating to form di-chlorides.

$SnCl_4(l) \rightarrow SnCl_2(s) + Cl_2(g)$

$PbCl_4(l) \rightarrow PbCl_2(s) + Cl_2(g)$

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HYDRIDES OF GROUP 4

CH_4	Methane
SiH_4	Silane
GeH_4	Germane
SnH_4	Stannane
PbH_4	Plumbane

The boiling points of the hydrides increase from methane down to stannane. This is due to increase in relative molecular mass. Thus the Van der Waals forces of attraction which bind the molecules together become progressively stronger as the relative molecular mass increases.

Methane, germane and stannane do not react with sodium hydroxide, but silane reacts with dilute sodium hydroxide to form sodium silicate and hydrogen gas.

$$SiH_4(l) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2SiO_3(aq) + 4H_2(g)$$

Ionically:$SiH_4(l) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3^{2-}(aq) + 4H_2(g)$

Hydrolytic behavior of hydrides of group 4

Methane does not under go hydrolysis due to absence of vacant d-orbitals.

Other hydrides are able to hydrolyse in water due to the availability of vacant d-orbitals which can accept electrons from the water molecules.

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$SiH_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4H_2(g)$

electr

water

$GeH_4(l) + 4H_2O(l) \rightarrow Ge(OH)_4(s) + 4H_2(g)$

$SnH_4(l) + 4H_2O(l) \rightarrow Sn(OH)_4(s) + 4H_2(g)$

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Carbon differs from other group 4 elements in the following ways:

- Its covalency is limited to 4 but others can have a maximum of 6. Due to absence of a vacant d-orbitals in carbon but others have.

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due to availability of vacant 'd'-orbitals which allows them to expand their

- Its unique ability to catenate. Due to its small atomic radius, the bonding electrons between two carbon atoms are closer to the nuclei and are attracted more strongly.
- Its unique ability to form multiple bonds such as: - ⁻C=C-, -C=C-, -C=N, etc.
- Its tetrachloride does not hydrolyze in water but tetra chlorides of other elements hydrolyze. Due to absence of vacant d-orbitals.
- Carbon is the only element in group 4 which forms only gaseous oxides.

Why carbon differs from other elements in group 4

- Very small atomic radius of carbon atom.
- High electro- negativity of carbon atom.
- Absence of vacant d-orbitals.
- Unable to show the inert pair effect

Qn.

When dilute hydrochloric acid is added to a solution of lead(ii) nitrate, a white precipitate is formed ,but if the concentrated acid is used, a much less precipitate is

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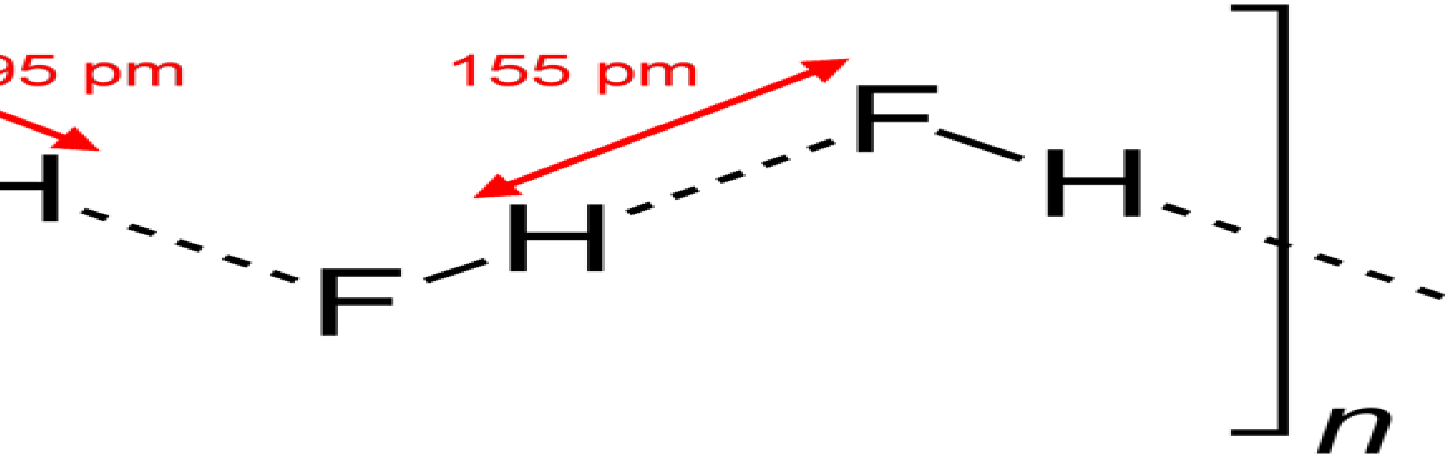
formed. Explain this behavior and write ionic equation for the reaction.

The Hydrides of period 3

Hydride	Formula
Sodium hydride	NaH
Magnesium hydride	MgH_2
Aluminium hydride	AlH_3
Silane	SiH_4
Phosphine	PH_3
Hydrogen sulphide	H_2S
Hydrogen chloride	HCl



<H-Cl< H-Br< H-I.

s very strong as a result of small atomic radius and high electronegativity

tween HF molecules and water molecules inhibits the ionization of HF in a

ivity decreases whereas atomic radius increases. As such the H- halide bor
re hydrogen ions.

lly decreases in moving from HF to HI i e *r gets more and more distant from the nucleus. The attraction is less, and t*

he smallest atomic radius thus the H-F bond is the most polar. Iodine is the
The greater the extent of polarity, the greater the ionic character in the bond

om other members of its group are:

er oxidation state. This because fluorine lacks empty d-orbitals but others h

gases at room temperature. This is due to the strong hydrogen bonds betwee

he hydrides of other members are fairly more acidic in aqueous solution. Th

ow bond dissociation energy and high electronegativity.

acter due to its high electronegativity and charge density of the small F^- ion oint in aqueous solution due to extensive hydrogen bonds .

al.

ge density, high polarising power, and high enthalpy of hydration.

es with increase in the number of oxygen atoms attached to chlorine atom.
d more towards itself.

greater the number of oxygen atoms attached the stronger the effect and th

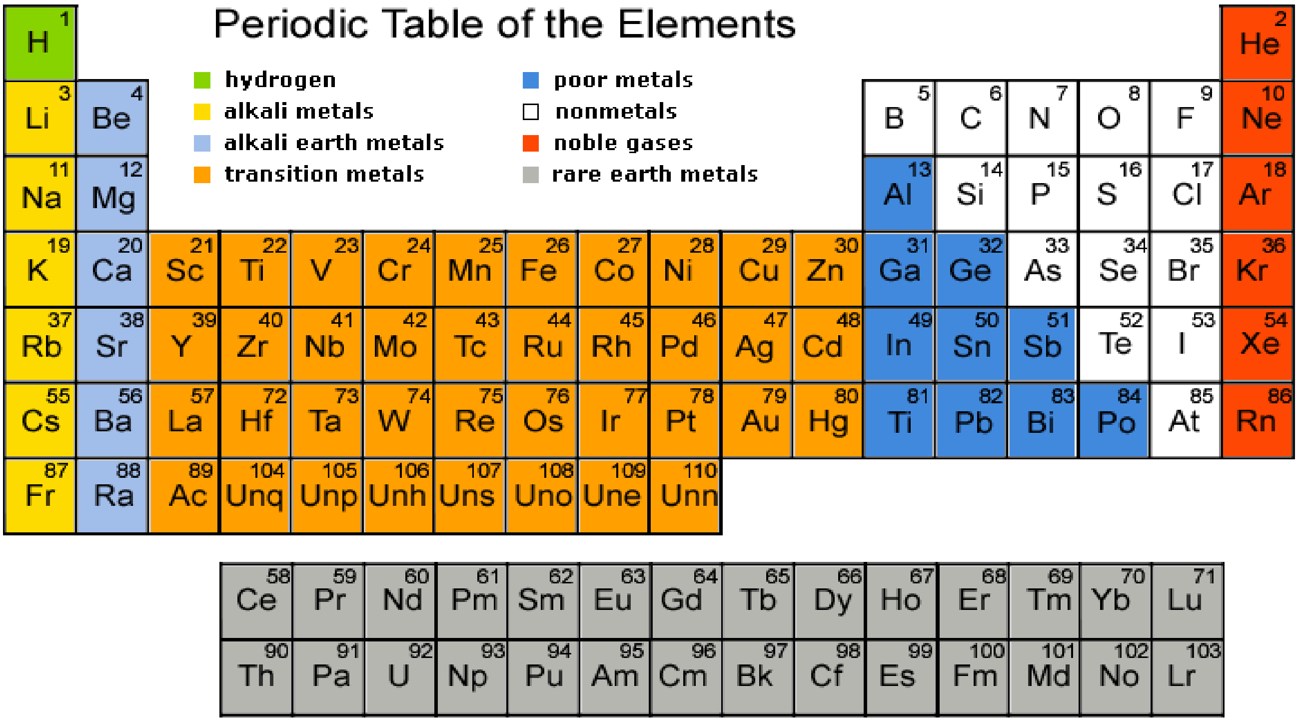
h of oxyacids above .

.

rine with the following substances(in each case illustrate your answer with

7. TRANSITION ELEMENTS

(Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc)



Periodic Table of the Elements

- 🟩 hydrogen
- 🟨 alkali metals
- 🟦 alkali earth metals
- 🟧 transition metals
- 🟦 poor metals
- ☐ nonmetals
- 🟥 noble gases
- ⬜ rare earth metals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

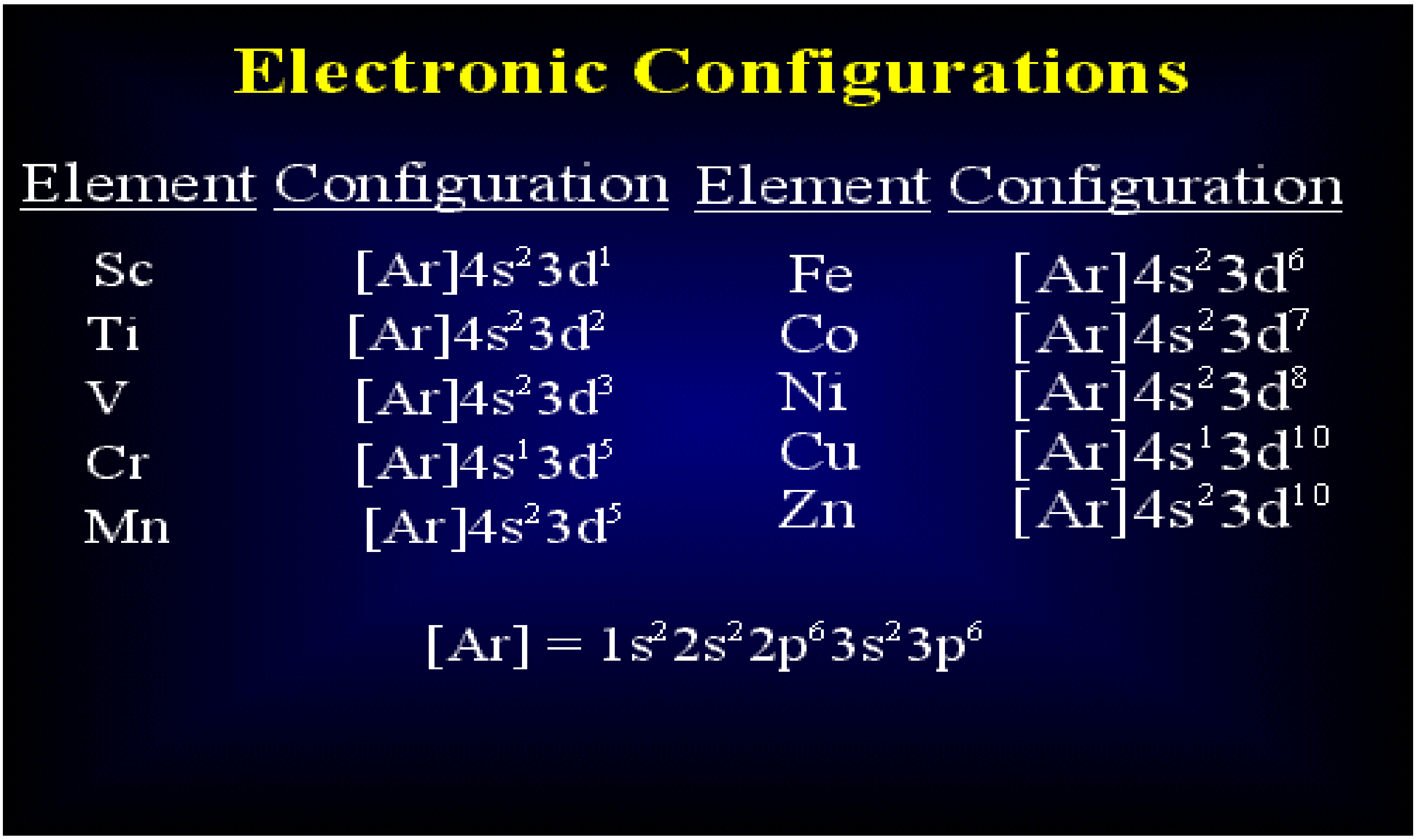
d-block elements:

A d-block element is one in which the inner ‘d’ sub-shell (which has a higher energy) is in the process of filling up after the outermost ‘s’ sub-shell(which has a lower energy) has been filled first.

In the periodic table, they are found between the very reactive s-block elements and the less reactive p-block elements.

Transition elements:

A transition element is one that has a partially filled d-orbitals either in the free atom in its ground state or in one or more chemically important ions.



Electronic Configurations

Element	Configuration	Element	Configuration
Sc	$[Ar]4s^2 3d^1$	Fe	$[Ar]4s^2 3d^6$
Ti	$[Ar]4s^2 3d^2$	Co	$[Ar]4s^2 3d^7$
V	$[Ar]4s^2 3d^3$	Ni	$[Ar]4s^2 3d^8$
Cr	$[Ar]4s^1 3d^5$	Cu	$[Ar]4s^1 3d^{10}$
Mn	$[Ar]4s^2 3d^5$	Zn	$[Ar]4s^2 3d^{10}$

$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

The sub shells are filled up in order of increasing energy and so the 4s-orbitals are filled 1st before the 3d-orbitals.

NB:

For chromium, the electronic configuration of $[Ar]3d^5 4s^1$ is a more stabl arrangement than $[Ar]\ 3d^4 4s^2$.

This is because the former configuration has **<u>more unpaired electrons</u>** than the latter and therefore more stable owing to half filled 3d-orbitals. Unpaired electrons experience minimum repulsion between each other .

For copper, the configuration $3d^{10}4s^1$ is a more stable arrangement than $3d^9 4s^2$. The explanation is because the 3d-subshell is full therefore its energetically stable.

CONFIGURATION OF SELECTED IONS

Sc^{3+}	
Cr^{3+}	
Mn^{2+}	
Mn^{3+}	
Fe^{2+}	
Fe^{3+}	
Cu^{+}	
Cu^{2+}	
Zn^{2+}	

When a transition metal atom loses electrons to form ions, the 4s-electrons are lost first before 3d-electrons.

This is because the 3d sub -shell is situated closer to the nucleus than the 4s sub shell.

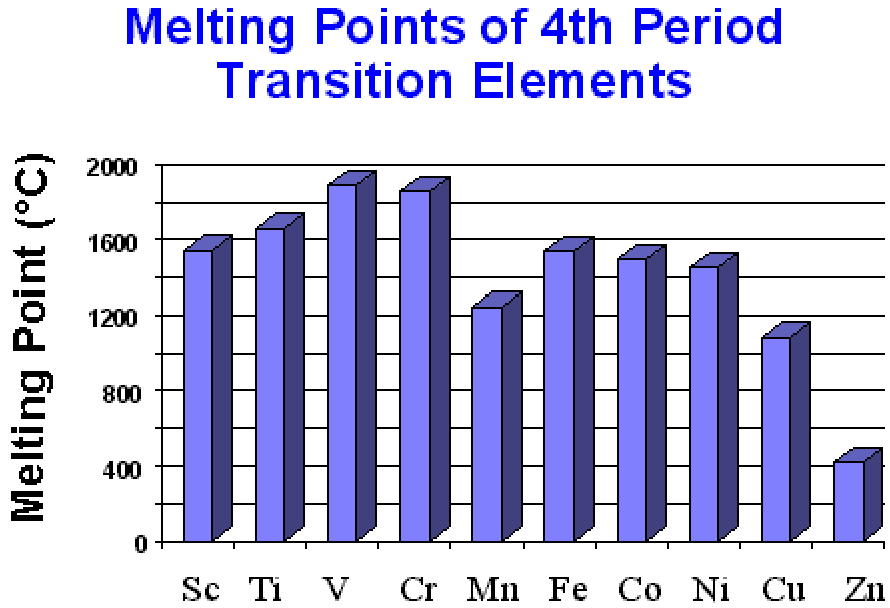
Thus when the 3d sub shell is occupied, the electrons in it repel the 4s-electrons further from the nucleus thereby increasing their energies than 3d-electrons and they are lost first.

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

1. **High melting and boiling points**.

Melting points of metals depend on the number of electrons available for metallic bond formation.

Transition elements use both the 4s and 3d-electrons on. in the metallic bond formation. The greater the number of electrons contributed to the metallic bonds , the higher the melting point. Hence they have high melting and boiling points.



The melting points of these metals rise to a maximum value and then decrease with increase in atomic number.

A dip in the melting point is observed at manganese $[Ar]4S^{2}3d^{5}$. This is attributed to the stability of a half-filled 3d-orbitals, electrons therefore being less available for bond formation.

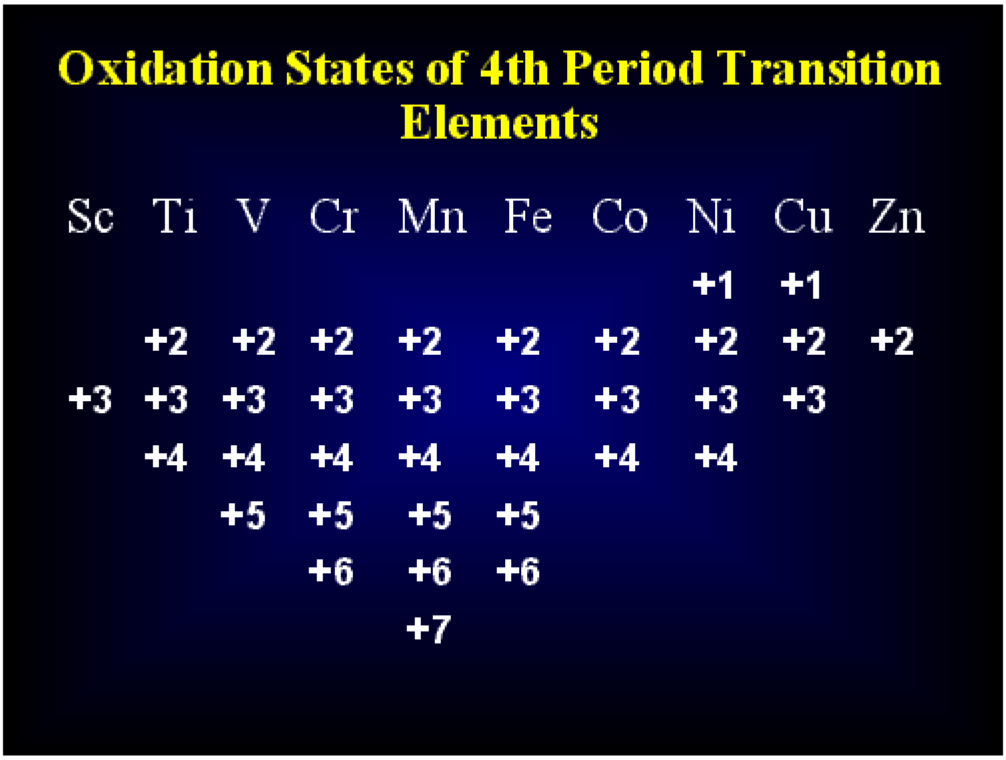
Zinc $[Ar]4S^{2}3d^{10}$ with a full 3d-orbitals uses only the outer most 4s-electrons in metallic bond formation as such has the lowest melting point.

2. Variable oxidation states.

The variable oxidation states exhibited by transition elements is attributed to the fact that both the 4s and 3d-electrons are energetically similar and they can both be used in bond formation.

All elements with exception of scandium and zinc show variable oxidation states. For an oxidation state of +2, only the outer most 4s-electrons are used in bond formation. For an oxidation state greater than +2, both the 4s and 3d-electrons are involved in bond formation.

The maximum oxidation state is achieved when all the 4s and 3d-electrons are involved in bonding.



Oxidation States of 4th Period Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

Workout the oxidation state of the transition metal in each of the following compounds or ions:

i) MnO_4^-

ii) MnO_4^{2-}

iii) MnO_2

iv) $Cr_2O_7^{2-}$

v) K_2CrO_4

vi) $Fe(CN)_6^{3-}$

3. Catalytic activity.

Transition metals and their compounds behave as catalysts due to the presence of partially filled d-orbitals .

The reacting gases are adsorbed onto the surface of the catalyst where they form weak bonds by either donating or accepting electrons. This weakens the internal bonding of the reactant molecules thereby reducing the activation energy.

Also there is a higher concentration of the reactants at the surface of the catalyst as a result the rate of reaction increases.

Some common examples include:

Haber process in the manufacture of ammonia, finely divided iron is used.

Contact process in the manufacture of sulphuric acid, vanadium pent oxide is used.

Decomposition of hydrogen peroxide , manganese(iv) oxide is used.

Hydrogenation of alkenes and alkynes, nickel metal is used.

4.Complex ion formation.

A complex ion basically consists of a central metal atom or ion surrounded by electron donating groups called ligands capable of forming dative covalent bonds with the metal atom or ion.

Complex ion formation in transition metals is affected by the following factors:

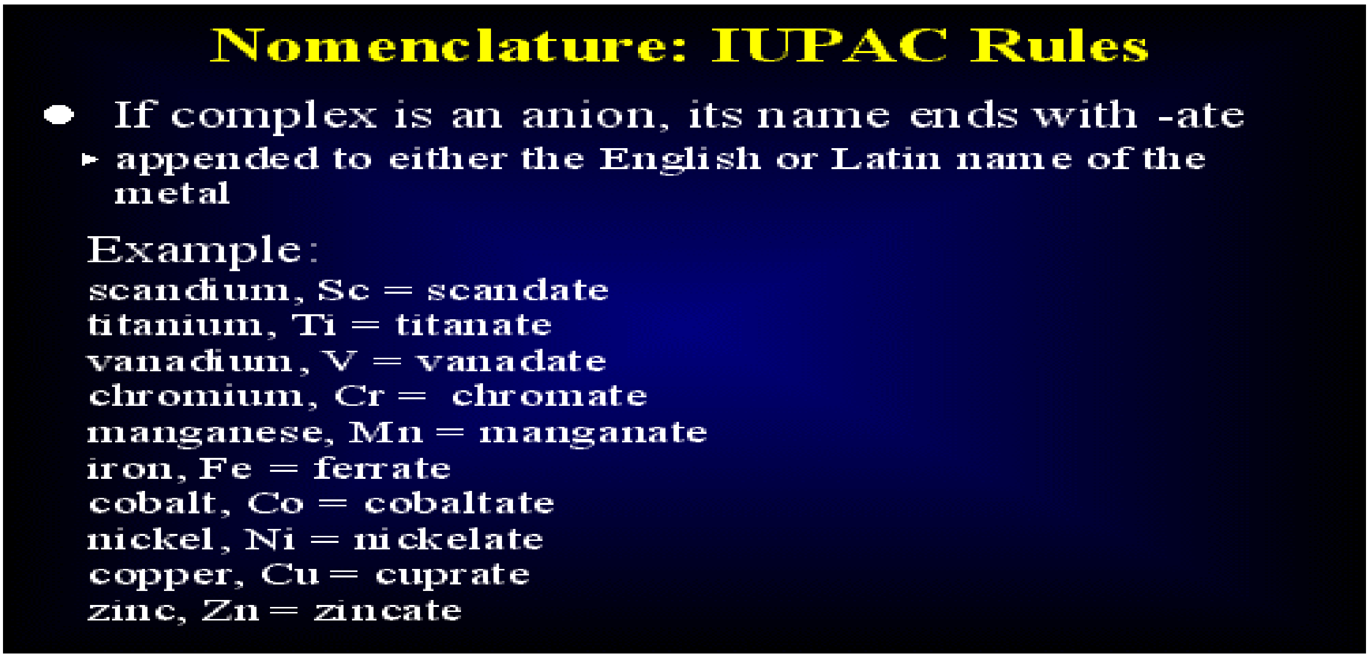
- presence of vacant d-orbitals.
- the high charge on the metal cation.)
- the small radius of the cation.

Example of a complex ion is $[Ni(H_2O)_6]^{2+}$, and is said to have a coordination number of 6.

Coordination number is the number of ligands directly bonded to the central metal ion. A complex species can be cationic, anionic or neutral.

Cationic complexes are those that carry an over all positive charge

Anionic complexes are those that carry a negative charge.



Nomenclature: IUPAC Rules

- If complex is an anion, its name ends with -ate
  - appended to either the English or Latin name of the metal

Example:

scandium, Sc = scandate
titanium, Ti = titanate
vanadium, V = vanadate
chromium, Cr = chromate
manganese, Mn = manganate
iron, Fe = ferrate
cobalt, Co = cobaltate
nickel, Ni = nickelate
copper, Cu = cuprate
zinc, Zn = zincate

Neutral complexes are those that carry no charge.

$Ni(CO)_4$, Tetracarbonylnickel(O)

$Fe(CO)_5$, Pentacarbonyliron(O)

Qn. Give the name, coordination number, and the oxidation state of the metal ions in the following complexes:

i) $Cr(H_2O)_6Br_3$ ii) $[Cr(H_2O)_6]Cl_3$ iii) $[Cr(H_2O)_5Cl]^{2+}$

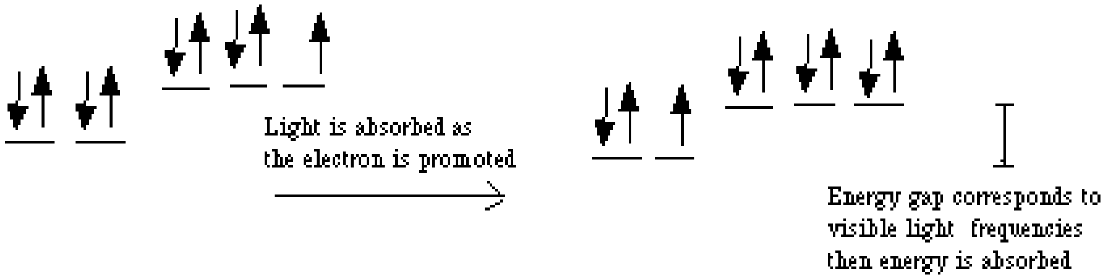
iv) $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$ v) $[Cr(H_2O)_4Cl_2]^+$.

5. **Form colored compounds**.

Transition metal ions are colored because they have partially filled 'd' sub shell.

A transition metal ion exhibits color when it absorbs light from the visible region.

Light in the visible region has sufficient energy to promote d-electrons from a lower energy level to a higher energy level.



6. **Magnetic Properties**

Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons in the molecule the stronger the attraction. This type of behavior is called paramagnetism.

Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called diamagnetism.

Many transition metal complexes exhibit simple paramagnetism. In such compounds the individual metal ions possess some number of unpaired electrons.

CHROMIUM

a) Write the electronic configuration of the following species (atomic

i)Cr

ii)Cr^{2+}

iii)Cr^{3+}

iv) Cr^{6+}

b) State the common oxidation states of chromium.

c) Aqueous sodium hydroxide was added drop wise to a solution containing Cr^{3+} ,state what was observed and write equation for the reaction that took place.

d) Discuss using equation where applicable the reactions of chromium with:

i) air

ii) water

iii) nitric acid ,hydrochloric acid and sulphuric acid .

Answers

a) i) Cr: $1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^1$

ii) Cr^{2+}:$1S^2 2S^2 2P^6 3S^2 3P^6 3d^4$

iii) Cr^{3+}: $1S^2 2S^2 2P^6 3S^2 3P^6 3d^3$

iv) Cr^{6+}:$1S^2 2S^2 2P^6 3S^2 3P^6$

NB

Chromium adopts the above electronic configuration rather than the expected $1S^2 2S^2 2P^6 3S^2 3P^6 3d^4 4S^2$ because the 3d is half filled unlike in the expected configuration therefore it’s more energetically stable.

b) +2, +3, +6

c) Observation

Green precipitate, soluble in excess to form deep green solution.

Equations

$Cr^{3+}{}_{(aq)} + 3\ OH^-{}_{(aq)} \rightarrow Cr(OH)_{3\ (s)}$

$Cr(OH)_{3\ (s)} + 3\ OH^-{}_{(aq)} \rightarrow Cr(OH)_6{}^{3-}{}_{(aq)}$

d)

i) With Air (oxygen)

Chromium does not react with oxygen at room temperature, when heated it forms green chromium (iii) oxide.

$4Cr_{(s)} + 3O_{2(g)} \rightarrow 2Cr_2O_{3(s)}$

green

ii) With water.

Chromium reacts with steam to form green chromium (iii) oxide and hydrogen gas.

$2Cr_{(s)} + 3\ H_2O_{(g)} \rightarrow Cr_2O_{3(s)} + 3H_{2(g)}$

iii) With acids.

Chromium reacts with dilute hydrochloric acid forming

- green chromium(iii) chloride solution and,
- Liberating hydrogen gas.

$2Cr_{(s)} + 6HCl_{(aq)} \rightarrow 2CrCl_{3(aq)} + 3H_{2(g)}$

- ✓ Chromium reacts with dilute sulphuric acid forming blue solution of chromium(ii) sulphate and liberating hydrogen gas.
- ✓ The blue solution turns to green when exposed to air. This is due to aerial oxidation of Cr^{2+} to Cr^{3+} ions.

$$Cr_{(s)} + H_2SO_{4(aq)} \rightarrow CrSO_{4(aq)} + H_{2(g)}$$

$$4CrSO_{4(aq)} + O_{2(g)} + 2H_2SO_{4(aq)} \rightarrow 2Cr_2(SO_4)_{3(aq)} + H_2O_{(l)}$$

Ionically:

$$\mathbf{Cr_{(s)} + 2H^+_{(aq)} \rightarrow Cr^{2+}_{(aq)} + H_{2(g)}}$$

$$\mathbf{4Cr^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \rightarrow 4Cr^{3+}_{(aq)} + 2H_2O_{(l)}}$$

- ✓ Chromium reacts with dilute sulphuric acid on heating to form chromium(iii) sulphate and hydrogen gas

$$2Cr_{(s)} + 3H_2SO_{4(aq)} \rightarrow Cr_2(SO_4)_{3(aq)} + 3H_{2(g)}$$

- ✓ Chromium reacts with hot conc. sulphuric acid to form chromium (iii) sulphate, sulphur dioxide and water.

$$2Cr_{(s)} + 6H_2SO_{4(aq)} \rightarrow Cr_2(SO_4)_{3(aq)} + 6H_2O_{(aq)} + 3SO_{2(g)}$$

NB: Chromium does not react with nitric acid due to the formation of a thin layer of chromium (vi) oxide which renders it passive towards nitric acid.

iv) With chlorine

If chlorine gas is passed over heated chromium, green solid of chromium (iii) chloride is formed.

$$2Cr_{(s)} \quad + \quad 3Cl_{2(g)} \quad \rightarrow \quad 2CrCl_{3(s)}$$

NB: If hydrogen chloride is used instead, chromium (ii) chloride is for

$$Cr_{(s)} + 2HCl_{(g)} \rightarrow CrCl_{2(s)} + H_{2(g)}$$

V) With sodium hydroxide solution.

Chromium dissolves to give:

- effervescence of a colorless gas that burns with a pop sound and
- a green solution is formed.

$$2Cr_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \rightarrow 2Cr(OH)_4{}^-_{(aq)} \quad + \quad 3H_{2(g)}$$

$$Cr(OH)_6{}^{3-}_{(aq)}$$

Compounds of Chromium

Chromium shows a principle oxidation states of +2, +3, & +6.

The most stable oxidation state of chromium is +3.

The acidity of the hex aqua ions

In aqueous solution, soluble salts of chromium in +3 oxidation state i.e. $CrCl_3$, $Cr(SO_4)_3$ etc exist as $[Cr(H_2O)_6]^{3+}$.

The resultant solution is acidic due to hydrolysis reaction.

$[Cr(H_2O)_6]^{3+}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [Cr(H_2O)_5OH]^{2+}{}_{(aq)} + H_3O^+{}_{(aq)}$

$[Cr(H_2O)_5OH]^{2+}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [Cr(H_2O)_4\ 2OH]^{+}{}_{(aq)} + H_3O^+{}_{(aq)}$

$[Cr(H_2O)_4\ 2OH]^{+}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [Cr(H_2O)_3 3OH]_{(s)} + H_3O^+{}_{(aq)}$

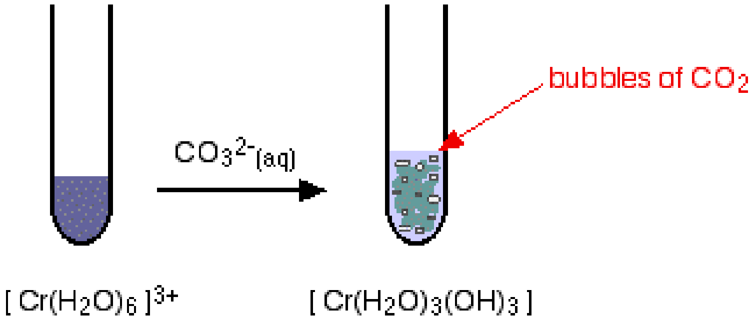
Over all equation:

$\mathbf{[Cr(H_2O)_6]^{3+}{}_{(aq)} + 3H_2O_{(l)} \leftrightarrow [Cr(H_2O)_3 3OH]_{(s)} + 3H_3O^+{}_{(aq)}}$

(Green ppt).

The hydroxonium ions produced make the resultant solution acidic with PH less than 7 and a green solid is formed.

If sodium carbonate solution is bubbled through aqueous solution of chromium (iii) salts, bubbles of a colorless gas that turns lime water milky is formed.



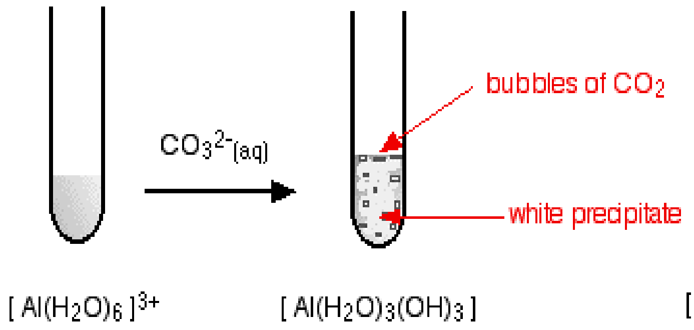
If magnesium ribbon is added to aqueous chromium (iii) salt, a colorless gas that burns with a pop sound is liberated.

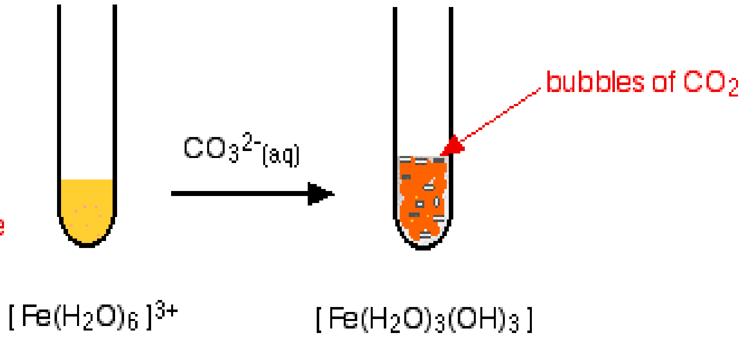
$$Mg(s) + 2H_3O^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) + 2H_2O(l)$$

or

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

Similar reactions occur with aqueous solution of Aluminium salts & iron (iii) salts.





Chromium(iii) oxide, Cr_2O_3:

It's a green solid which can be obtained by heating chromium (iii) hydroxide.

$$2Cr(OH)_{3(s)} \rightarrow Cr_2O_{3(s)} + 3H_2O_{(l)}$$

Its amphoteric, reacts with dilute mineral acids to form corresponding Cr^{3+} salt and with sodium hydroxide to form complex.ie

$$\mathbf{Cr_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3H_2O_{(l)}}$$

$$\mathbf{Cr_2O_{3(s)} + 6OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Cr(OH)_6^{3-}{}_{(aq)}}$$

(Green solution).

Chromium(iii) hydroxide

It's a green solid formed when little sodium hydroxide is added to a solution of Cr^{3+} ions. It's an amphoteric hydroxide, reacts with dilute acids forming corresponding Cr^{3+} salts and with aqueous alkalis forming a complex species.

$Cr(OH)_{3(s)} + 3H^+_{(aq)} \rightarrow Cr^{3+}_{(aq)} + 3H_2O_{(l)}$

$Cr(OH)_{3(s)} + 3OH^-_{(aq)} \rightarrow Cr(OH)_6{}^{3-}_{(aq)}$ ***Chromite ion***

NB:

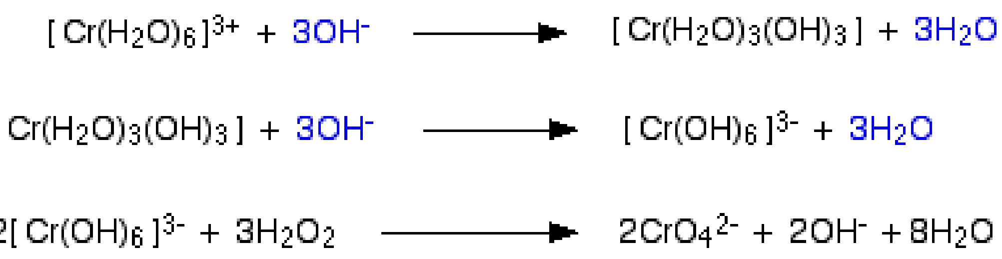
Chromium (iii) hydroxide is oxidized by hydrogen peroxide solution in an alkaline medium to form chromate ion. i.e.

Addition of sodium hydroxide drop-wise till excess to a solution containing Cr^{3+} ions followed by a little H_2O_2 and boiling the resultant solution.

<u>Observation:</u>

A green precipitate soluble in excess, forming green solution. The solution turns yellow on addition of hydrogen peroxide.

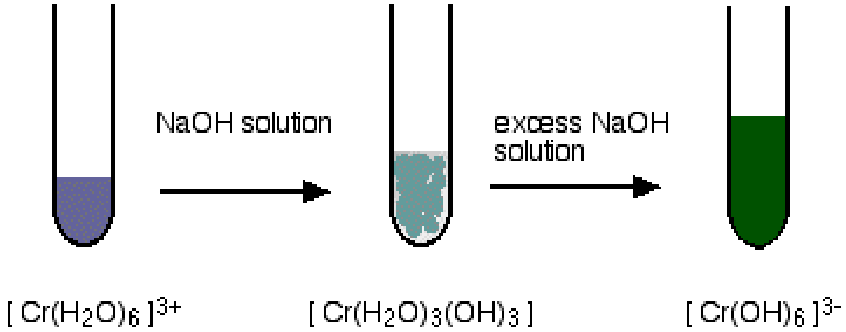
Equation:

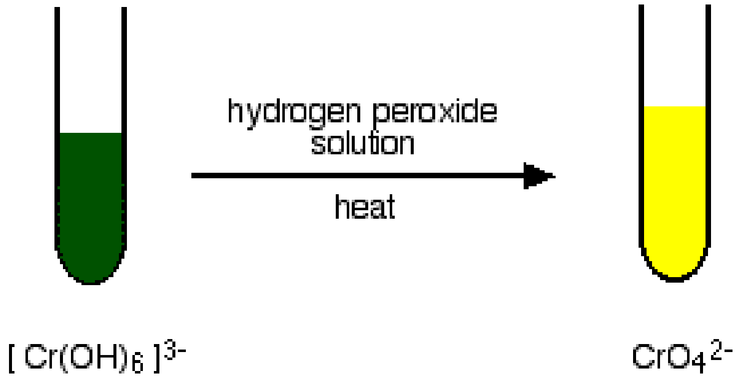


$[Cr(H_2O)_6]^{3+} + 3OH^- \longrightarrow [Cr(H_2O)_3(OH)_3] + 3H_2O$

$Cr(H_2O)_3(OH)_3] + 3OH^- \longrightarrow [Cr(OH)_6]^{3-} + 3H_2O$

$2[Cr(OH)_6]^{3-} + 3H_2O_2 \longrightarrow 2CrO_4{}^{2-} + 2OH^- + 8H_2O$





OR

$$Cr^{3+}_{(aq)} + 3\,OH^-_{(aq)} \rightarrow Cr(OH)_{3\,(s)}$$

$$Cr(OH)_{3(s)} + 3OH^-_{(aq)} \rightarrow Cr(OH)_6^{3-}{}_{(aq)}$$

$$2\,Cr(OH)_6^{3-}{}_{(aq)} + 3H_2O_{2\,(aq)} \rightarrow 2CrO_4^{2-}{}_{(aq)} + 2\,OH^-_{(aq)} + 8H_2O_{(l)}$$

The presence of the chromate ions produced can be confirmed by:

- Addition of Lead (ii) ethanoate or Lead (ii) nitrate solution.

Observation

A yellow precipitate is formed.

Equation

$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow PbCrO_{4(s)}$

- Addition of Barium nitrate or Barium chloride solution.

Observation

A yellow precipitate is formed

Equation

$Ba^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow BaCrO_{4(s)}$

- Addition of silver nitrate solution.

Observation

A brick red precipitate is formed.

Equation

$2Ag^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow Ag_2CrO_{4(s)}$

- Addition of a little amyl alcohol (eg Butan-1-ol) followed by dilute sulphuric acid.

Observation

A blue color is observed in the organic layer.

Hydrated Chromium(iii) Chloride.$CrCl_3.6H_2O$

This salt of chromium exhibits hydration isomerism i e existence of compounds with the same molecular formula but different structural formulae.

The following are the isomers of hydrated chromium(iii) chloride:

$[Cr(H_2O)_6]^{3+}\ 3Cl^-$

(Hex-aqua-chromium(iii) chloride)

$[Cr(H_2O)_5Cl]^{2+}.2Cl^-.H_2O$

(Chloropentaqua chromium(iii) chloride monohydrate)

$[Cr(H_2O)_4Cl_2]^{+}.Cl^-.2H_2O$

(Dichlorotetra-aqua chromium(iii) chloride dihydrate)

Identification/test of the isomers

1. **Using silver nitrate solution**:

- The first isomer precipitates 3moles of silver chloride because all the $3Cl^-$ ions are not directly bonded to the central metal cation,

- The 2nd isomer precipitates 2moles of silver chloride.
- The 3rd isomer precipitates 1mole of silver chloride.

2. **Using conductivity measurement**:

This test provides the number of moles of conducting ions in solution for every mole of isomer.

- The 1st isomer contains 4moles of conducting ions i.e. $[Cr(H_2O)_6]^{3+}$ and $3Cl^-$
- The 2nd isomer contains 3moles of conducting ions i.e. $[Cr(H_2O)_5Cl]^{2+}$ and $2Cl^-$
- The 3rd isomer contains 2moles of conducting ions i.e. $[Cr(H_2O)_4Cl_2]^+$ and Cl^-

Compounds of chromium in +6 oxidation states

Because of the high charge density of Cr^{6+} ion, it can only exists as Oxo- ions.eg , CrO_3

, CrO_4^{2-} , $Cr_2O_7^{2-}$

CHROMATES ,CrO_4^{2-}

Chromates are salts of chromic acid, they have a characteristic yellow color. eg

K_2CrO_4 and Na_2CrO_4. It has a tetrahedral structure

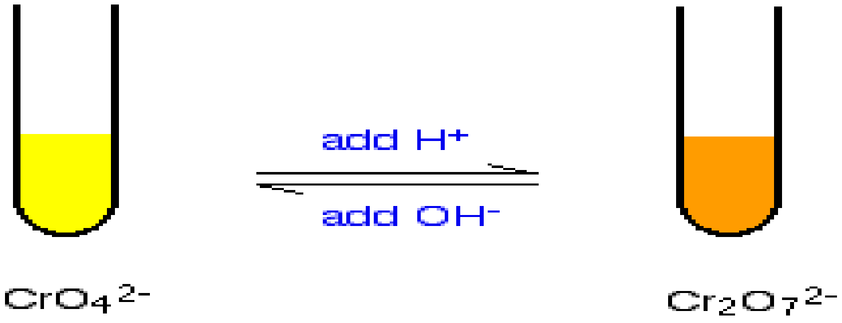
Chromates are obtained when an alkaline solution is added to a solution of dichromate ions.

$$Cr_2O_7^{2-}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow 2\,CrO_4^{2-}{}_{(aq)} + H_2O_{(l)}$$

Orange yellow

Chromates are stable in alkaline medium, however Chromates react with acids to form dichromate.

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \rightarrow Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$



MS

e double sulphate salts with general formula $M_2SO_4.M_2(SO_4)_3.24H_2O$

I is a group (I) metal e.g ***Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Rb^{+} , Cs^{+}*** etc

M is a group (III) metal or a metal bearing a +3 charge e.g ***Al^{3+} , Cr^{3+}, Fe***

s of common alums are:

alum $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

on in water is acidic because the chromium (iii) ions undergo hydrolysis le

plex ion is acting as an acid by donating a hydrogen ion to water molecule

ter is, of course, acting as a base by accepting the hydrogen ion.

$$)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightarrow [Cr(H_2O)_5OH]^{2+}_{(aq)} + H_3O^{+}_{(aq)}$$

$$)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightarrow [Cr(H_2O)_4\ 2OH]^{+}_{(aq)} + H_3O^{+}_{(aq)}$$

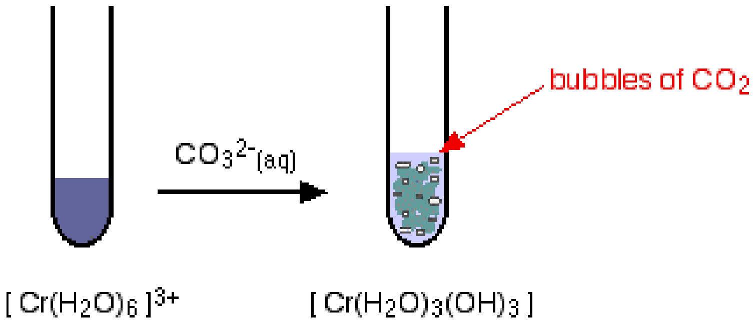
$$)_4\ 2OH]^{+}_{(aq)} + H_2O_{(l)} \rightarrow [Cr(H_2O)_3\ 3OH]_{(s)} + H_3O^{+}_{(aq)}$$

equation:

$$)_6]^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow [Cr(H_2O)_3\ 3OH]_{(s)} + 3H_3O^{+}_{(aq)}$$

nium ions renders the resultant solution acidic.

f a colorless gas which turns lime water milky is formed and a greeen solic

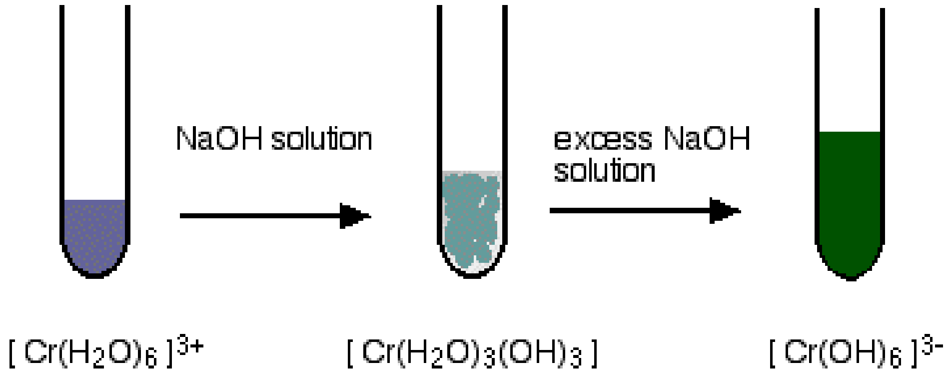


d potassium dichromate, chrome alum is formed.

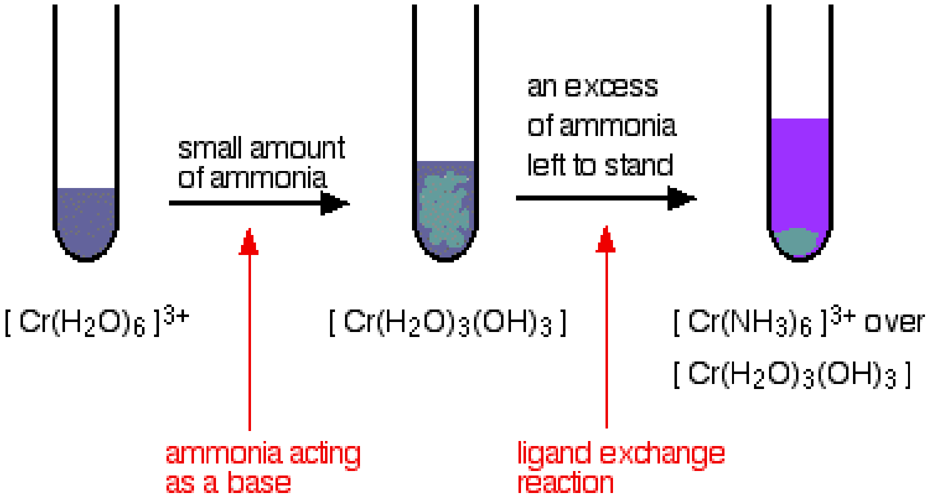
(aq) + 2e

t proportion for the formation of chrome alum on crystallizing.

en solution.



ed ammonia solution to form a purple solution.



m & Lead

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g)

d Pb^{4+} form covalent compounds e.g $PbCl_4$ and $CrCl_6$

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ZINC

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rities.

frothing agent) so as to remove the unwanted earthly materials. The oil we

The oiled sulphide particles float on the surface while the impurities sink to zinc oxide.

eated in a blast furnace.

ide.

to form calcium silicate (slag).

t coke to carbon monoxide. The carbonmonoxide reduces zinc oxide to zin

the zinc produced leaves as vapor at the top of the blast furnace where its c

REACTIONS OF ZINC

e. This layer prevents further reaction with the oxygen present in air.

drogen gas.

rming salt and hydrogen gas.

rogen gas.

products.

nc.) are not easily defined.

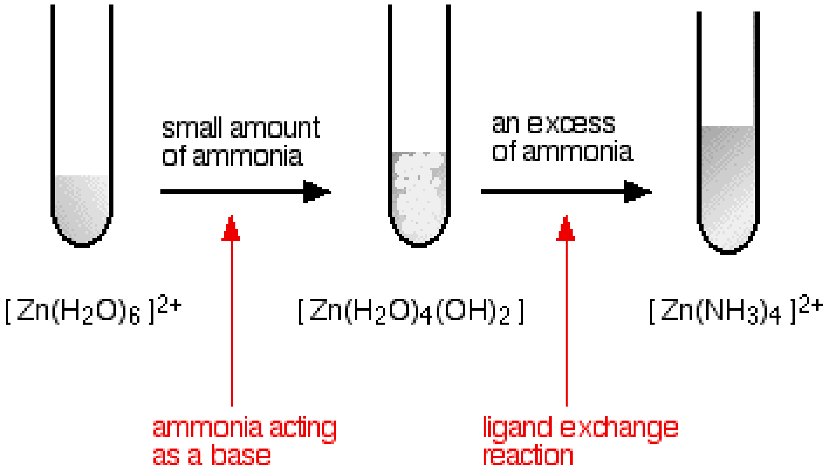
and hydrogen gas.

COMPOUNDS OF ZINC

odium hydroxide or aqueous ammonia to a solution containing zinc ions.

hydroxide to form sodium zincates’ complex.

colorless solution of tetra amine zinc ion.



ide through a solution of zinc ions.

lt, a metallic sulphide is formed but if the H_2S is passed through an acidic

ied, the excess H+ ions present suppresses the formation of sulphide ions i

sis of $[Zn(H_2O)_6]^{2+}$

+ H_3O^+(aq),

olution of Zn^{2+} ions produces a white ppt which dissolves in excess to form

f zinc ions, produces a white ppt soluble in excess to form a colorless solut

n of Zn^{2+} ions produces a white ppt. soluble in sodium hydroxide.7

hite ppt soluble in dilute HCl acid.

ed with zinc ions.

es .

the iron is exposed, iron does not rust.

d iron undergoes oxidation in preference to iron forming a thin layer of Zn

IRON

1st roasted in air to convert them to stable iron(iii) oxide. e.g

blast furnace

y pipes called Tuyeres located at the lower part of the furnace. The other m

ACE

xide gas

to form carbonmonoxide

a(SiO_2)

sent as impurities to form slag.

e and they can be tapped off separately. The molten iron is at the bottom co

Bunsen burner bases, boiler plates etc

ed the converter and air is blown into it to oxidize the impurities such as car

id of tri-iron tetra oxide.

n(iii) oxide or rust.

hen different parts of iron act as anode and cathode.

nydroxide is formed.

)

oxide.

gen gas and iron(ii) salts.

sulphur dioxide and water.

$H_2O(aq)$

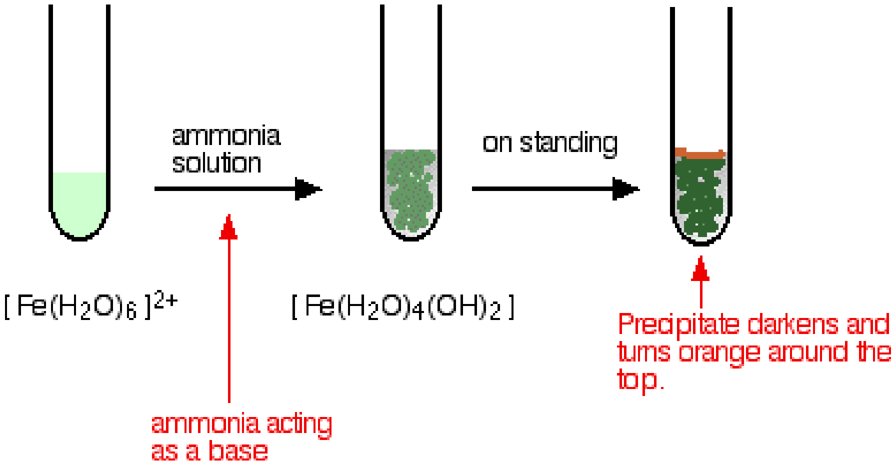
hloride.

solution. It undergoes hydrolysis making the resultant solution acidic.

n is added drop wise to a solution of Fe^{2+} solution. The ppt is insoluble in e

)

o aqueous Fe^{2+} solution



cid and crystallizing the salt from solution.

te forms as green crystals.

$O_2(g)$

acidic fumes

olution turns to yellow/ brown due to formation of iron(iii) ions.

$^{3+}$ and undergo hydrolysis in water making resultant solution acidic.

rolysis in aqueous solution to release hydrogen ions or hydroxonium ions t

$H_3O^+_{(aq)}$

iron(iii), the color of the solution changes to green.

olution of standard potassium permanganate.

+5Fe^{3+} (aq)

g Fe^{3+} ion, the color of the solution changes from yellow to green with forr

form oxide and hydrogen gas.

ydrogen gas.

e.

loride.

ron does not.

riable valencies of +2 &+3.

e forms compounds which are colored.

-subshell) while Zn is diamagnetic(due to paired electrons in its 3d-subsh moist air to form hydrated iron(iii) oxide (rust).

esium.

COPPER

e is then mixed with water and oil(frothing agent). The earthly materials si
washed and dried.

er(i) sulphide, iron(ii) oxide and sulphur dioxide.

d silica added. On strong heating, the iron(ii)oxide reacts with silica to for

(i)oxide.

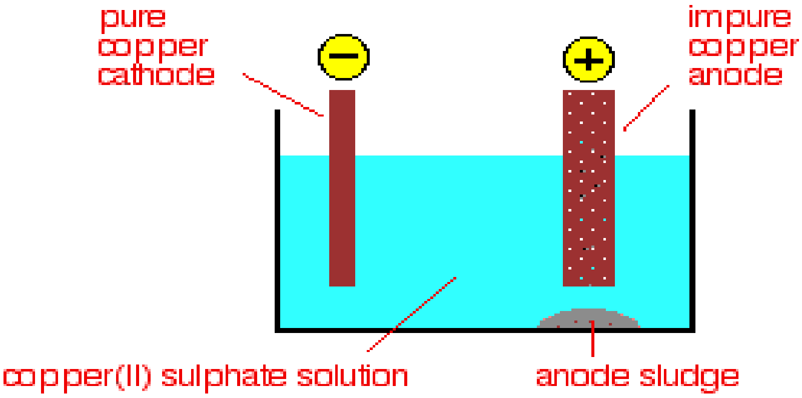
er(i)sulphide react in the heat of the blast furnace with limited air supply t

er copper and contains impurities . The last process in the extraction is puri

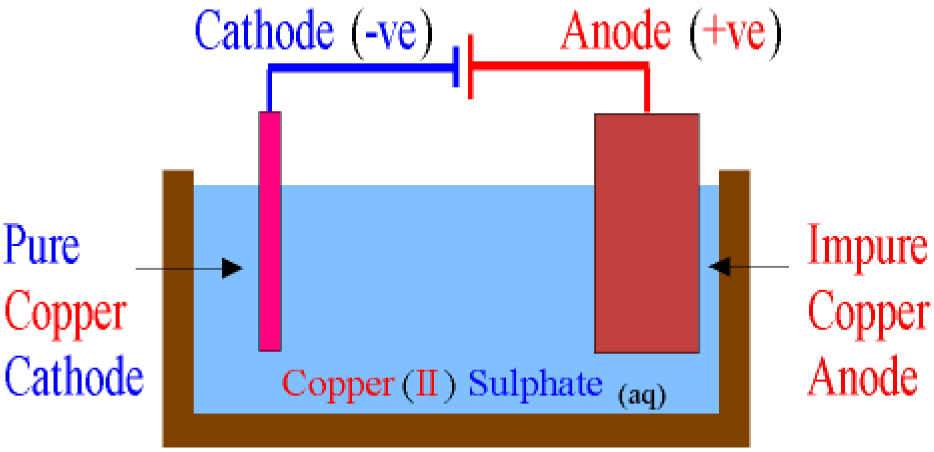
les is mixed with water and oil and shaken for a while.

ereas the ore particles (low density) float on the surface, where they are re g to copper.

sis.



or



olution.

Uses of copper

city and is easily drawn out into wires.

easily bent into shape.

heat and doesn't react with water.

roduces a metal harder than either copper or zinc individually. Bronze is a copper alloys - this time with nickel. These are known as cupronickel allo

copper(ii)carbonate(protective layer).

°C) to form black copper(ii) oxide.

gen to form copper(i)oxide.

e.

e.

trate, nitrogen monoxide and water.

)

per(ii)nitrate, nitrogen dioxide gas and water.

$2H_2O(l)$

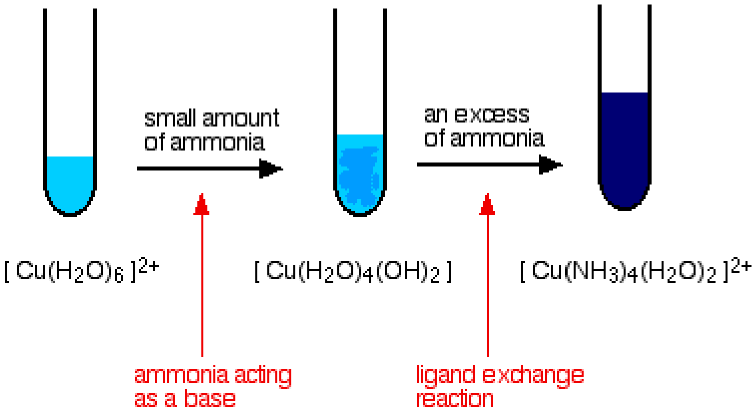
copper(ii) sulphate, sulphurdioxide and water.

ompounds in +1 oxidation state are unstable.

ueous solution exists as $[Cu(H_2O)_4]^{2+}$ which is a blue solution.

added to copper(ii) ions.

ydroxide. However dissolves in excess ammonia solution to form a deep b



eated copper metal.

o form a yellow solution of tetra-chlorocupprate(ii) ions $[CuCl_4]^{2-}$

its ligands are replaced by a different ligand which is more willing to dona
nge.

$Cu(NH_3)_4]^{2+}$

Deep blue

ER(II) SALTS

ric acid)

otassium iodide, a white precipitate of copper(i) iodide is formed which is ing the resultant solution with a standard solution of sodium thiosulphate u

two equations above :

.

that of copper ions present in the solution can be determined.

l)

potassium iodide solution followed by dilute sulphuric acid .

berated iodine is then titrated with a standard solution of sodium thiosulph

MANGANESE

ies (atomic number= 25):

eason for your answer.

.

olution containing Mn^{2+} ,state what was observed and write equation for th

in an oxidation state of

on state?

owing similarities.

er using the 4s-electrons, a half filled 3d -orbital that is stable is left.

asing oxidation state.

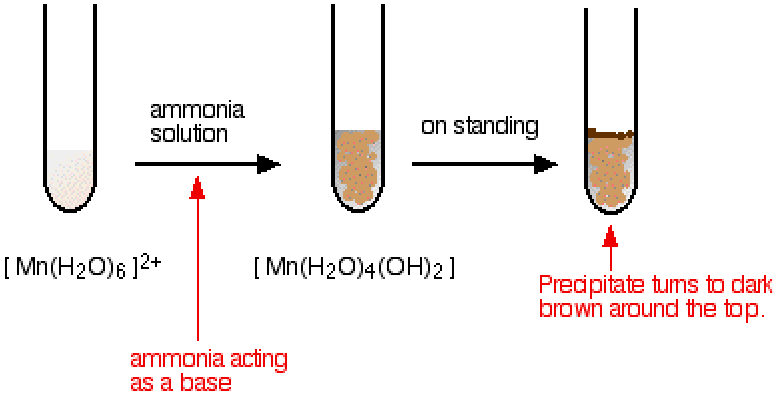
e fact that both the 4s and the 3d- electrons take part in bond formation.

cally similar 4s and 3d- orbitals.

r bond formation, forming stable Mn^{2+}. For higher oxidation states, both t

wn due to aerial oxidation .

onia solution.



on state of +7 by using both the 4s and 3d- electrons in the bond formation

$^+7$ to $^+4$ since potassium manganate (vii) is a mild oxidizing agent in alkal

s an oxidizing agent which include the following:

ints of titrations.

n conc hydrochloric acid is reacted with it.

ration because $KMnO_4$ is a very strong oxidizing agent, oxidizes Cl^- ions fr

) $+8H_2O_{(l)}$

heated.

nitrides

o liberate hydrogen gas.

Magnesium react with steam in the same way.

solution.

entrated nitric acid and little solid lead (IV) oxide or sodium bismutha

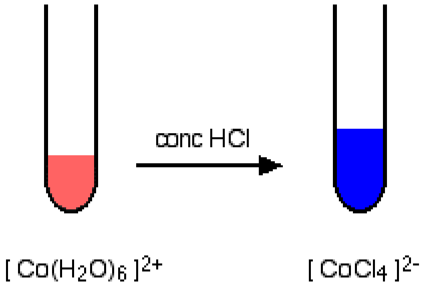
$O_{4}^{-}{}_{(aq)} + 5Bi^{3+}_{(aq)} + 7H_2O_{(l)}$

${}_{(aq)} + 5Pb^{2+}_{(aq)} + 2H_20_{(1)}$

e for simple cobalt salts; they are colored pink . The simplest ion t

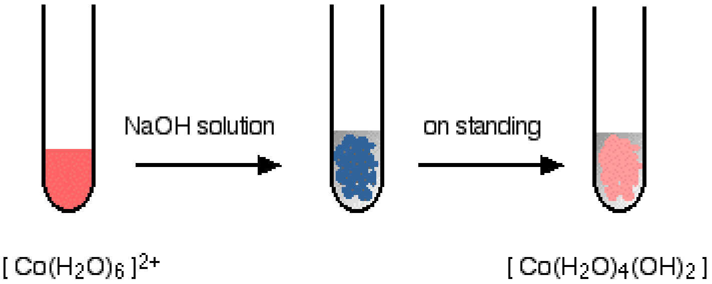
de ions

o a solution containing hexaaquacobalt(II) ions, the solution turns fro
ide ions.



rns to the pink colour.

ss and turns pink on standing



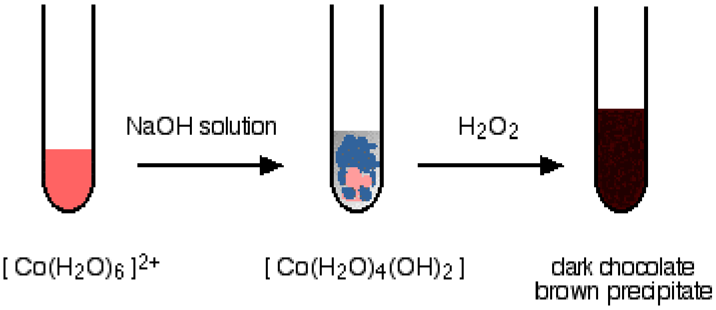
Precipitate changes colour on standing

gen peroxide

you can add an oxidising agent such as hydrogen peroxide

hen you add the sodium hydroxide solution.

ts of bubbles of oxygen and a dark chocolate brown precipitate.



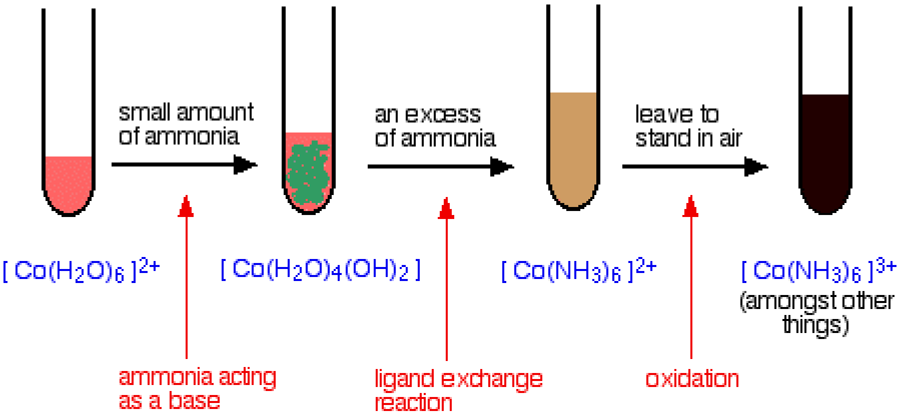
+3 oxidation state.

(s)

n excess to form a brown solution and turns to a deep red -brown so

$^{2+}{}_{(aq)}$ + $2\ OH^-_{(aq)}$

aq) + e



xide

you can add an oxidising agent such as hydrogen peroxide

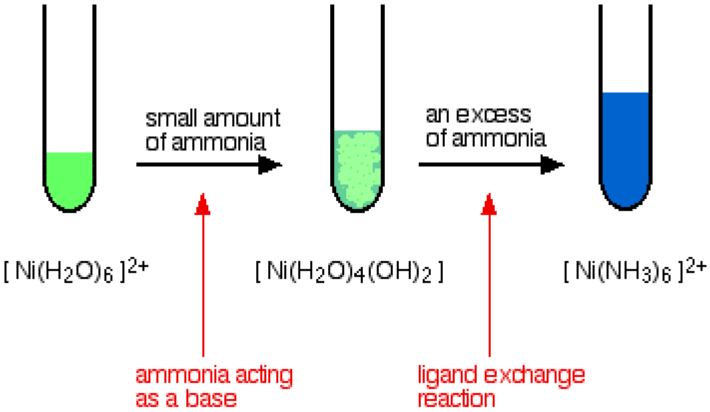
ed by hydrogen peroxide produces the same dark reddish-brown sol

OH^-

med.

in excess to form a blue solution

$+ 2OH^-_{(aq)}$



ia solution drop-wise until excess followed by a drop of dimethylglyc

nd red precipitate is formed .