Introduction:

Inorganic chemistry is a branch of chemistry concerned with substances that contain little or no carbon. A few of the carbon compounds are however conventionally included in inorganic chemistry.

Inorganic chemistry embraces all the elements of the periodic table, their physical and chemical properties, their occurrence in the earth's crust etc. Inorganic Chemistry therefore deals with all topics except a part of carbon chemistry, which is dealt with under organic chemistry.

Early studies in inorganic chemistry were directed towards solving analytical and mineralogical problems. There is, too, a mass of relatively factual information concerning the preparation, manufacture, properties factual and uses of inorganic chemicals.

For effective study of Inorganic chemistry, you are advised to have a copy of the periodic table to guide you.

Chapter one

ELECTRONIC CONFIGURATION OF ATOMS:

This refers to the arrangement of electrons in atoms.

Within an atom, electrons are arranged in shells/energy levels around the central part of an atom called the nucleus.

The energy levels are numbered *1,2,3,4* etc or *k, l, m, n etc*, with *1* or *k* being the shell nearest to the nucleus.

With the exception of the first energy level, the other shells are divided into sub- energy levels/sub shells.

Within the shells, electrons are found in what is referred to as orbitals.

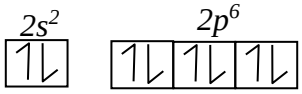
An orbital is a volume or space around the nucleus within the shells where electrons are found.

1) The 1st energy level has only one orbital called ***1s*** and like any other **s** orbital can take a maximum of two electrons.

   $1S^2$

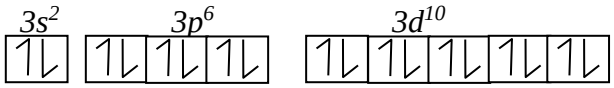
   Therefore when full the 1st shell has 2 electrons.
2) The 2nd energy level has 2 sub shells called the ***2s*** and ***2p***.
   The ***2s*** sub shell takes in a maximum of two electrons because it has one orbital.
   The ***2p*** sub shell like any other *p* sub shell has 3 orbitals and when full has 6 electrons.

   $2s^2$ $2p^6$

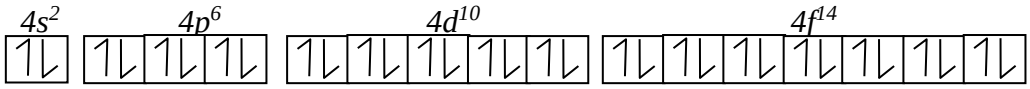
   

   Therefore the maximum number of electrons that can be accommodated within the 2nd shell of any atom is 8.
3) The 3rd energy level has 3 sub shells, namely *3s, 3p* and *3d*.
   The ***3s*** takes in up to 2 electrons.
   The ***3p*** takes in up to 6 electrons and the ***3d*** shell like any other d sub shell consists of 5 orbitals and takes up to 10 electrons when full.

Therefore the maximum number of electrons that can be accommodated within the 3rd shell of an atom is 18.



4) The 4th energy level has 4 sub shell given denoted by *4s*, *4p*, *4d* and *4f*.
The 4s sub shell has one orbital and takes in up to 2 electrons.
The *4p* sub shell has 3 orbitals and can have up to 6 electrons when full.
The *4d* sub shell has 5 orbitals and has up to 10 electrons when full.
The *4f* sub shell has 7 orbitals and when full accommodates 14 electrons.



Therefore the maximum number of electrons that can be accommodated within the fourth shell of an atom is 32.

Note:
From the 4th shell onwards there are 4 sub shells, namely *s*, *p*, *d* and *f*.
For e.g. the 5th shell has *5s*, *5p*, *5d* and *5f* as its sub shells.

Rules for writing electronic configurations of atoms:

1. *Pauli Exclusion Principle*.

It states that an orbital can take in a maximum of two electrons on a condition that the electrons have parallel and opposite spins.$A = \pi r^2$

2. *Hund's Rule of maximum multiplicity*

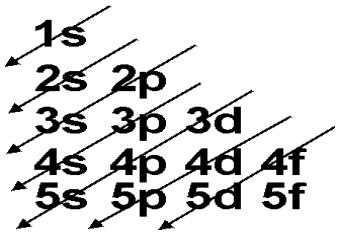
It States that when electrons are present in a number of degenerate orbitals (orbitals with more or less equal energy) they occupy all the orbitals singly first with parallel spins before pairing can occur in any one orbital.

3. *Aufbau pattern of filling energy level*

It States that electrons fill in the sub shells in order of increasing energy beginning with the sub shell of lowest energy, followed by that of second lowest energy and so and so forth.

After filling the second energy level, the first in a series of several overlap of energy occurs between the *3d* and the *4s* sub energy levels. The *3d* sub shell though nearer to the nucleus than the *4s* sub shell happens to be at a higher

energy level therefore the electrons are filled in the *4s* sub energy level before filling the *3d* sub shell. After filling the *4s* sub shell, electrons then fill the *3d* energy level.



Aufbau pattern of filling energy levels

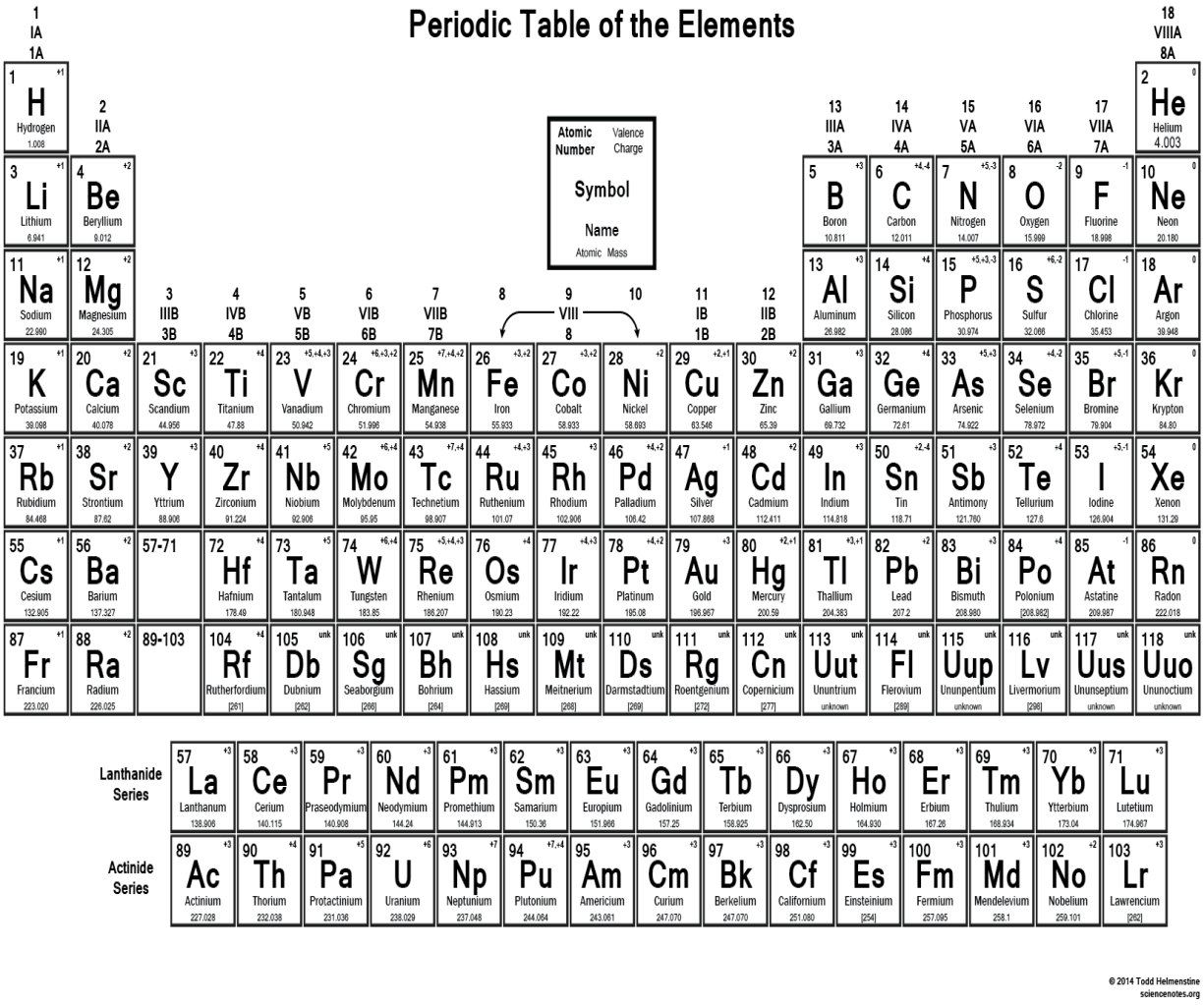
Testing Exercise 1

Write the electronic configuration of the following elements with their respective atomic number (Z)

c) Aluminium (Z=13)
d) Phosphorous (Z=15)
e) Calcium (Z=20)
f) Chlorine (Z=17)
g) Vanadium (Z=23)

Chapter 2

THE MODERN PERIODIC TABLE OF ELEMENTS:



History of the development of the periodic table:
The development of the periodic classification of the chemical elements was a stepping stone in the evolution of Chemistry.

In the 19th century, when chemists had only a vague idea of atoms and molecules and did not know of the existence of electrons and protons, they devised a table commonly called the periodic table using their knowledge of

atomic masses. Arranging elements according to atomic masses in the periodic table seemed logical to these scientists who felt that chemical behavior was somehow related to atomic masses.

In 1864, an English Chemist, **John Newlands** noticed that when the known elements by then were arranged in order of increasing atomic mass, every first and eighth element had similar properties (The noble gases were still unknown).
Newlands therefore referred to this peculiar relationship as the "law of octaves". His proposal had similarity with music where the eighth note is an octave above the first note.
However his law turned out to be inadequate for elements beyond calcium. His work therefore was not accepted by the scientific community.

Five years after the work of Newlands (1864-1869) a Russian Chemist, **Dmitri Mendeleev** proposed a much extensive tabulation of the elements based on the regular, periodic recurrence of properties.
Although the development was carried through Mendeleev, an independent development was carried through by a German Chemist **Lothar Meyer**.
Mendeleev like Lothar summarized his findings in what is called Mendeleev periodic law.
His law states that both physical and chemical properties of elements are a periodic function of their atomic masses.
However, Atomic mass as a basis for arranging elements was found to be unsatisfactory due to inconsistencies such as;

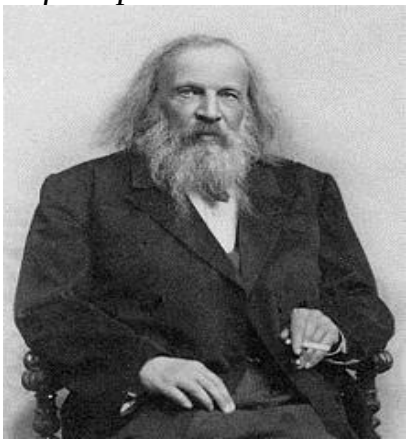
- No satisfactory place for hydrogen was given.
- The rare earth elements, the lanthanides and actinides were not provided for.

In that same year, a young English Physicist by the names **Henry Mosley** observed that the frequency of X- rays emitted from the elements followed atomic numbers not atomic weights.
Mosley stated the periodic law as; *"The chemical and physical properties of elements are a periodic function of their atomic numbers."*

Until today, the modern periodic table, in which elements are arranged according to their atomic numbers, shows a great success in grouping of the elements. This is because atomic number indicates the number of electrons in the atom and this determines the physical and chemical properties of the elements.

Scientists that contributed to the development of the periodic table:

John Newlands



Dmitri Mendeleev

Henry Mosley

Format of the periodic table:

The Modern periodic table consists of two major divisions; namely

- The Vertical arrangement of elements referred to as the *Groups* which consist of elements with characteristic electron arrangement in the outer most shell. The Group are numbered using roman numerals for example: Group I, Group II, Group III……
- The Horizontal arrangement of elements referred to as the *Periods* which are classified depending on the number of electrons on the outer most shell

With so many elements, it is impractical to do a study of each one individually. The elements here will first be classified generally as metals and nonmetals. Metals will be further divided into alkali and alkaline earth metals. Metalloids will be discussed as elements with intermediate properties of metals and nonmetals, with metals on the left side of the periodic table and nonmetals on the right.
Metals are found on the left side of the table with the most active metal in the lower left corner. Nonmetals are found on the right side with the most active nonmetal in the upper right hand corner of the chart. The noble or inert gasses are on the far right. Since the most active metals react with water to form bases, the Group I metals are called alkali metals. As you proceed to the right, the base-forming property decreases and the acid forming properties increase. The metals in the first two groups are the light metals, and those toward the center are called heavy metals. The elements found along the dark line in the periodic table are called metalloids

Alkali Metals are the elements in Group IA of the periodic table. The members of the family are lithium, sodium, potassium, rubidium, cesium, and francium. All six elements have the properties of metals except they are softer and less dense. They can be cut with a knife. They are the most reactive metals. They are so reactive that they are never found in nature. They are always combined with other elements. The alkali metals have only one electron in their outermost shell, so alkali metals form positive ions.

Alkaline Earth Metals are beryllium, magnesium, calcium, strontium, barium, and radium. These elements, which are harder and denser than the alkali metals, also have higher melting points and boiling points. They are highly reactive, but not as active as the alkali metals. Like the alkali metals, the alkaline metals are never found free in nature. The alkaline earth metals have two electrons in their outermost energy level, so they also form positive ions.

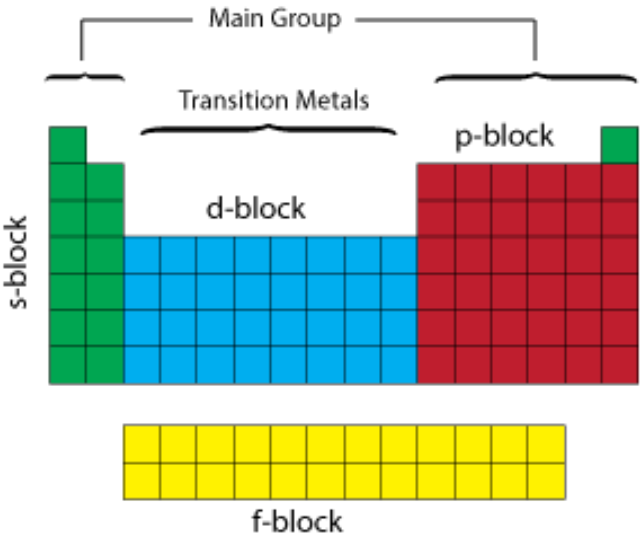
Transition Metals
These have properties similar to one another and to other metals, but their properties do not fit in with those of any other family. Most transition metals are excellent conductors of heat and electricity. Most have high melting points and are hard. Transition metals are much less active than the alkali and alkaline earth metals. Many transition metals combine chemically with oxygen to form compounds called oxides. Many transition metals have more than one oxidation number. Transition metals form compounds that are brightly colored

The Carbon family includes the elements carbon, silicon, germanium, tin, and lead. Carbon can combine with other elements in a great variety of ways. Millions of carbon compounds called "organic compounds" are known. Carbon is called the basis for life because all living things contain organic compounds. Silicon is the second most abundant element in the earth's crust. Silicon is used in glass and in cement. It is also used in solar cells. Solar cells convert the energy of sunlight into electric energy.
Germanium is a metalloid used in transistors. Transistors are devices found in many electronic instruments, such as radios and televisions. Tin is a metal which resists rusting and corrosion. The densest element in the carbon family is the metal lead. Lead forms poisonous compounds.

Halogens are the elements in group VIIA. They are strongly nonmetallic. The halogens include fluorine, chlorine, bromine, iodine, and astatine. They are the most active nonmetals. The chemical reactivity of the halogens is due to the number of electrons in the outermost energy levels of their atoms. Fluorine is the most active halogen. The elements have low melting points and boiling points. In the gas phase they exist as diatomic elements. Halogens combine readily with metals to form a class of compounds known as salts.

Noble Gasses are colorless and are extremely un-reactive. Because they do not readily combine with other elements to form compounds, the noble gasses are called inert. The family of noble gasses includes helium, neon, argon, krypton, xenon, and radon. All the noble gasses are found in small amounts in the earth's atmosphere. One important property of the noble gasses is their inactivity. They are inactive because their outermost energy level is full.

Blocks in the periodic table:
The periodic table splits into four regions depending on the type of orbitals that are being filled.
The regions are called s- block, p-block, d-block and f-block.



s-block elements:
These are elements with partially or completely filled outer s-orbital. It consists of elements in Group I and Group II having atoms containing 1s or 2s electrons in their outer orbitals for example:

H $1s^1$
Li $1s^2$
Na $1s^2 2s^2 2p^6 3s^1$
} All in Group I

Be $1s^2 2s^2$
Mg $1s^2 2s^2 2p^6 3s^2$
Ca $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
} All in Group II

p-block elements:
These are elements with partially or completely filled outer p-orbital. The block consists of Group III to Group VIII elements.
For example:

B	$1s^2 2s^2 2p^1$	Group III
C	$1s^2 2s^2 2p^2$	Group IV
N	$1s^2 2s^2 2p^3$	Group V
O	$1s^2 2s^2 2p^4$	Group VI
F	$1s^2 2s^2 2p^5$	Group VII
Ne	$1s^2 2s^2 2p^6$	Group VIII

d-block elements:

These are elements with partially or completely filled 3-d orbital. The d-electrons are being added to the penultimate energy level because the highest energy electrons are found in the 3d subshell.
For example:

Sc $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Ti $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Cu $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Zn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

f-block elements:
These are elements with partially or completely filled f-orbital. The electrons enter the antepenultimate energy level.
These elements are found in period 6 and form the inner transitional series.
For example:
Ho $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{11}$

NOTE: The vertical columns of elements in the d-block and f-block are not assigned group numbers.

Chapter 3

PERIODIC PROPERTIES OF ELEMENTS (PERIOCICITY):

Periodicity:
This usually refers to the recurrence or repetition of the resemblance of physical or chemical properties of elements in a particular group when the elements are arranged according to a given order.

Periodic property:
This is the property whose resemblance shows recurrence among a group of elements when the elements are arranged according to some particular order. For chemical elements, the arrangement is according to atomic number.
These properties are:

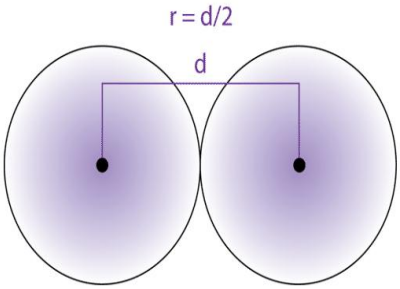
a) Atomic radius
b) Ionic radius
c) Ionisation energy
d) Electronegativity
e) Electropositivity
f) Electron affinity
g) Melting point
h) Boiling point
i) Density
j) Electrode potential

ATOMIC RADIUS:

Definition:
This is the distance of closest approach from the nucleus of an atom to another identical atom in a bonding situation.

The bonding situation is metallic bonding if the two identical atoms are metal atoms and if the identical atoms are non metals, the bonding situation is covalent bonding.
At such a distance, the sum of the inter-electronic and the inter-nuclear repulsions just balance the nuclear–electronic attraction.
Alternative definition
Atomic radius is half the inter-nuclear distance between two identical atoms in a bonding situation.
Still the bonding situation is covalent if the two identical atoms are covalent atoms and metallic bonding for two identical metallic atoms.

Illustration:



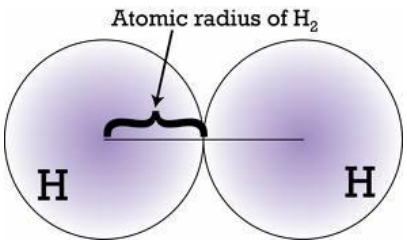
NOTE:

The above definitions for atomic radius are based on the fact that it is practically impossible to measure the radius of an independent atom.

This is because electrons do not have definite orbits, or sharply defined ranges.

Depending on the definition, the term may apply only to atoms covalently bound in molecules, or in ionized and excited states; and its value may be obtained through experimental measurements, or computed from theoretical models.

It is therefore important for you to understand atomic radius as the distance from the center of the nucleus of an atom to the outermost shell, however, defining atomic radius this way is unacceptable in chemistry.



Factors determining the radius of an atom of an element:

1) *Nuclear charge.*

This is the total Charge of all protons in the nucleus of an atom.

The nuclear charge is determined by the number of protons present in the nucleus of an atom e.g. sodium atom with 11 protons in its nucleus has a nuclear charge of +11.

Increase in the nuclear charge of an atom leads to a decrease in atomic radius. This is attributed to the increased attraction of the nucleus for the electrons present in the shells, pulling them closer to it (nucleus) hence leading to a decrease in atomic radius.

Decrease in nuclear charge results into an increase in atomic radius.
This is attributed to the decreased attraction of the nucleus for the electrons present in the shells, weakly attracting them which results into electrons being far away from the nucleus hence leading to an increase in atomic radius.

2) *Screening (shielding) effect*.

This is the repulsion of the outermost electrons (valence electrons) by the electrons in the inner shells.
Shielding electrons are electrons that are in energy levels between the nucleus and the valence electrons. These electrons shield the valence electrons from the force of attraction exerted by the positively charged nucleus.

Down the group, the screening effect majorly increases with the increase in the number of shells down the group except for transitional metals.
Across the period, the screening effect remains relatively constant because electrons are added to the same valence shell from one element to the next across the period.

Increase in screening effect on the outer most electrons increases the atomic radius and the decrease in screening effect on the outermost electrons decreases the atomic radius.

VARIATION OF ATOMIC RADIUS IN THE PERIODIC TABLE:

Note:

Variation of atomic radius in the periodic table is explained in terms of the factors affecting it; nuclear charge and screening effect therefore they should appear in your answer to qualify to be correct.

Generally

Atomic radius *Increases* down the group while it (atomic radius) *decreases* across the period.

Across the period from one atom to the next, there is an increase in nuclear charge as protons are being added to the nucleus of the atoms but the shielding (screening) effect of the electrons in the inner shell(s) on the electron(s) in the outermost shell remains more or less constant because electrons are being added to the same shell.
As a result the effective nuclear charge increases and electron(s) in the outer most shell is increasingly attracted more strongly to the nucleus leading to a decrease in atomic radius.

Down any group in the periodic table, both the nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge because of an extra shell of electrons added from one element to the next one.
The effective nuclear charge therefore decreases i.e. the nuclear attraction for the outer most electron(s) decreases leading to an increase in atomic radius.

Examples;

1. *Consider Group IA elements (Alkali metals).*

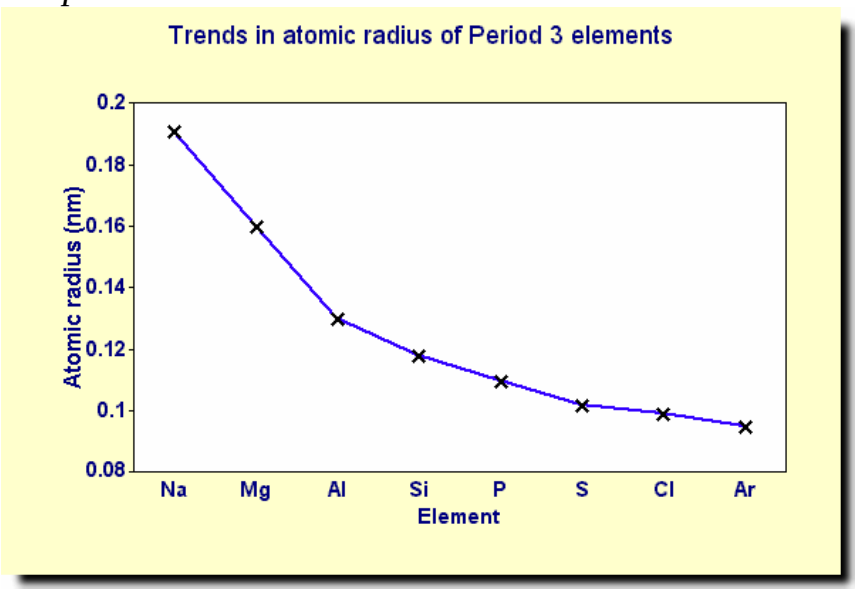
Atomic radius of group 1 elements:

Element	*Atomic Number*	*Electronic configuration*	*Atomic radius /^{0}A*
Li	*3*	$1s^2 2s^1$	*1.52*
Na	*11*	$1s^2 2s^2 2p^6 3s^1$	*1.54*
K	*19*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	*2.27*
Rb	*37*	$1s^2 2s^2 2p^6 3^{s2} 3p^6 4s^2 3d^{10} 4p^6 5s^1$	*2.48*
Cs	*55*	--------	*2.65*

Trend:
Atomic radius generally increases from sodium to the next elements up to caesium down the group.

Explanation:
Down any group in the periodic table, both the nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge because of an extra shell of electrons added from one element to the next one.
The effective nuclear charge therefore decreases i.e. the nuclear attraction for the outer most electron(s) decreases leading to an increase in atomic radius.

2. *Consider period 3 elements*



Trend:
Atomic radius decreases across the periods from sodium up to Argon

Explanation:
Across the period from one atom to the next, there is an increase in nuclear charge as protons are being added to the nucleuses of the atoms but the shielding effect of the electrons in the inner shell(s) on the electron(s) in the outermost shell remains more or less constant because electrons are being added to the same shell.

As a result the effective nuclear charge increases and electron(s) in the outer most shell is increasingly attracted more strongly to the nucleus leading to a decrease in atomic radius.

3. *Consider transitional elements:*

Element	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
Atomic number	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**
Atomic Radius	**0.160**	**0.146**	**0.131**	**0.125**	**0.129**	**0.126**	**0.125**	**0.124**	**0.128**

Trend:
Atomic radius remains almost constant.

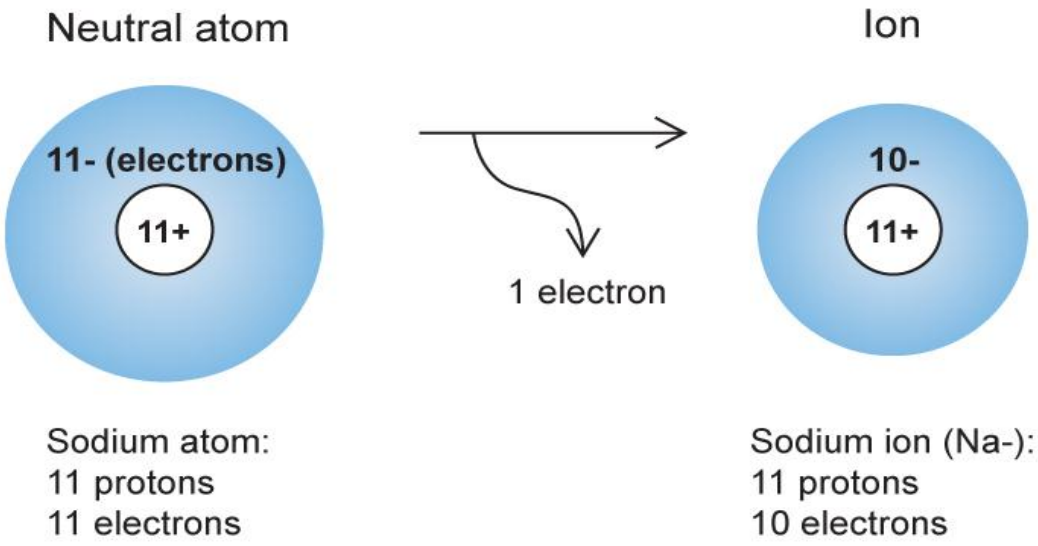
Explanation:
Across the transitional elements, nuclear charge increases as protons are added to the nucleus of the atoms but this increase is roughly balanced by the greater screening effect produced as the number of electrons in the 3d-subshell increase.
The effective nuclear charge remains roughly constant (slightly increases) across the transitional element series. This results into no significant change in the atomic radius of elements across the transitional elements series.

IONIC RADIUS:

This is half the inter-nuclear distance between two neighboring mono atomic ions in an ionic crystalline salt where the ions are held together in a single ionic bond.

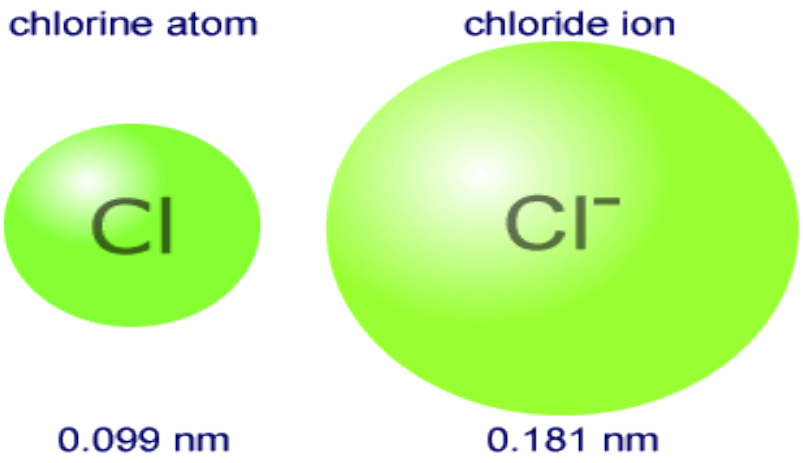
Ions are atoms that have either lost or gained electrons. Metallic elements lose electrons and as such they form cations while non-metals gain electrons and form anions.
Ionic radius therefore can be described as cationic radius for cations or anionic radius for anions.

The radius of a cation is smaller than the radius of the atom from which it's formed.



Explanation:
After the loss of one or more electrons by an atom, the number of protons in the nucleus becomes 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.

The radius of an anion is larger than that of the atom from which it is 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 now electrons now decreases leading to increase in anionic radius.

Variation of Ionic radius across the period:

Both cationic and anionic radius decrease across the period.

> **Note:**
> Due to each atom's unique ability to lose or gain an electron, periodic trends in ionic radius are not as definite as trends in atomic radii across the period

Consider the following examples:

1. *Cationic radius in period 3 elements: sodium, magnesium, and Aluminum.*

Ion	**Na^+**	**Mg^{2+}**	**Al^{3+}**
Ionic radius(nm)	0.095	0.065	0.050

Explanation:

From sodium to Aluminium, nuclear charge increases due to the addition of protons in the nucleus.

Also, from sodium to aluminium, the number of electrons lost from the respective ions increases from 1 to 3 forming ions with the same number of electrons and thus the same degree of electron-electron repulsion and shielding with differing number of protons. This results into an increased effective nuclear charge because the increased nuclear charge attracts the same number of electrons from sodium ion to aluminium ion hence consequently reducing the ionic radius from sodium ion to aluminium ion.

2. Anionic radius in period 3 elements

Ion	**P^{3-}**	**S^{2-}**	**Cl^-**
Ionic radius(nm)	0.212	0.184	0.181

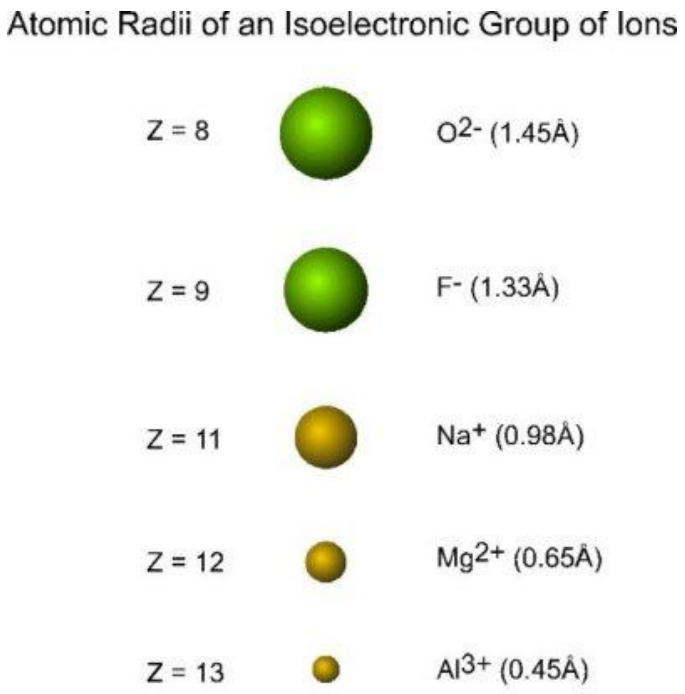
Explanation:

From phosphorous to chlorine, nuclear charge increases because of the addition of protons in the nucleus of atoms; however, the number of electrons gained from the respective ions reduces from 3 to 1, forming ions with the same number of electrons thus the same degree of shielding but with differing number of protons which increase from phosphide to chloride ions.

This results into an increased effective nuclear charge, hence decreasing anionic radius from phosphide ion to chloride ion.

Isoelectonic Ions:

Isoelectronic ions are ions with the same electronic configuration.



Explanation:

Al^{3+},Mg^{2+},Na^{+}, F^{-} all 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 has the highest proton-electron ratio and therefore the strongest nuclear attraction for the electrons.

Therefore Al^{3+} has the smallest ionic radius.

IONIZATION ENERGY:

Definition:

Ionization energy is the energy required to remove one mole of electrons from one mole of gaseous atoms of a given element to form one mole of gaseous ions.

$$M_{(g)} \rightarrow M^{+}_{(g)} + e \qquad \Delta H = \text{Ionization energy}$$

NOTE:

Valence electrons (electrons in the outer most shell) are removed first when ionizing an atom.

First Ionization energy:

This is the enthalpy change when one of electrons is removed from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions of the element.

$$M_{(g)} \rightarrow M^{+}_{(g)} + e \qquad \Delta H = \text{First ionization energy}$$

For example

For a sodium atom,

$$Na_{(g)} \rightarrow Na^{+}_{(g)} + e \qquad \Delta H = +494 KJMol^{-1}$$

Second ionization energy:

Is the minimum energy required to remove one mole of electrons from one mole of unipositively charged gaseous ions to form one mole of dipositively charged gaseous ions of the element.

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

For example:

For a sodium ion;

$$Na^{+}_{(g)} \rightarrow Na^{2+}_{(g)} + e \Delta H = +4560 KJmol^{-1}$$

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

For example, it is more difficult to remove the 2nd electron in sodium than the 1st electron as can be seen from the 1st and 2^{nd}ionization energies values above.

FACTORS THAT DETERMINE THE MAGNITUDE OF IONIZATION ENERGY:

Since electrons are bound to the nucleus or in an atom by the effective nuclear charge; all factors that affect the magnitude of effective nuclear charge affect the magnitude of ionization energy. These factors include:

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius
4) Electronic configuration of the atom
5) Penetrating power of valence electrons
6) Net charge on the atom or ion

Explanation:

Nuclear charge:
If the nuclear charge of an atom is high, then the electrons present in the outer most shell of that atom experience a high nuclear attraction.
Therefore removing an electron from the atom requires more energy leading to high 1st ionization energy.
For a low nuclear charge, the electrons present in the atom experiences a low attraction from the nucleus of such an atom leading to low 1st ionization energy.

Shielding effect of the electrons in the inner shells:
If the screening effect by the electrons in the inner shells on the electrons in the outermost shell is high, then the outermost electron experiences a low nuclear attraction leading to low 1st ionization energy.
If the screening effect on the outermost electron is low, then electron experiences a high nuclear attraction leading to a high 1st ionization energy value.

Atomic radius.
If the radius of an atom is small, then the outer most electrons are closer to the nucleus and thus experience a high nuclear attraction leading to high 1st ionization energy.
If the radius of an atom is large, the outer most electrons are further away from the nucleus and hence experiences a low nuclear attraction leading to low 1st ionization energy value.

Electronic configuration of the outer most shell
When the first electron being removed is from an atom whose electronic configuration is stable (*e.g. N:* $1s^2 2s^2 2p^3$ *or Ne;* $1s^2\ 2s^2\ 2p^6$), a lot more of

energy is needed to remove the 1st electron leading to a high 1st ionization energy.
But if the 1st electron being removed is from an atom whose electronic configuration is thermodynamically less stable (*e.g. O;* $1s^2 2s^2 2p^4$) then less energy is required to remove the 1st electron from such an atom i.e. the 1st ionization energy value is low.

Penetrating power of valence electrons:
This is the measure of how close electrons in a given subshell are to the nucleus. In any given subshell; the penetrating power of electrons decreases in the order s>p>d>f.
Therefore, s- electrons are more penetrating than p-electrons and the trend continues. The electrons that are closest to the nucleus are more strongly held; consequently in a given shell, Ionisation energy increases in the order s>p>d>f.

Net charge on the atom or ion:
Ionization energy increases with increase in charge on the ion because as electrons are removed, the nuclear charge remains constant but the number of electrons reduce. This results into an increased effective nuclear charge; increasing the attraction of electrons more strongly to the nucleus which inturn increase the ionization energy.

Variation in first ionization energy down a group in the periodic table:

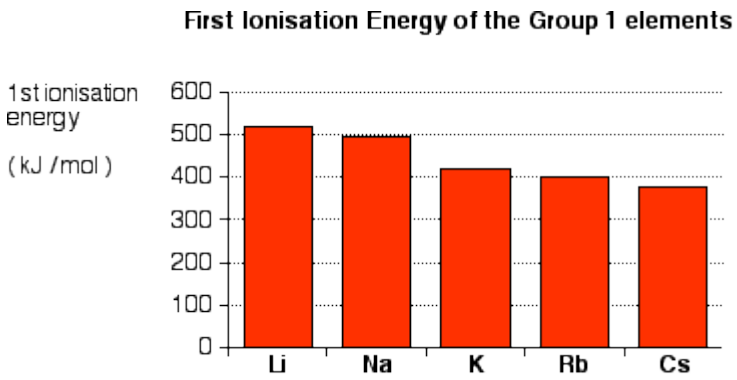
Generally:
Trend:
Ionization energy increases across the period and decreases down the group.

Explanation:
Down a group in the periodic table a full shell is added from one atom to the next one therefore both the nuclear charge and screening effect increase, but the increase in screening effect on the electrons in the outer most shell by the electrons in the inner shells outweighs the increase in nuclear charge.
This leads to a decrease in the effective nuclear charge and hence the nuclear attraction for the outer most electrons decreases making the removal of the outer most electron require less energy. i.e. 1st ionization energy generally decreases.

Across the period in the periodic table from one atom to the next one, an electron is being added to the outermost shell and also the next atom has one more proton in its nucleus compared with the previous atom. The nuclear charge therefore increases while the screening effect of the electrons in the inner shell on the outer most electrons remains approximately constant.

These leads to an increase in the effective nuclear charge leading to an increase in the nuclear attraction for the outer most electron and hence increase in 1st ionization energy.

Examples:
Consider group IA elements.

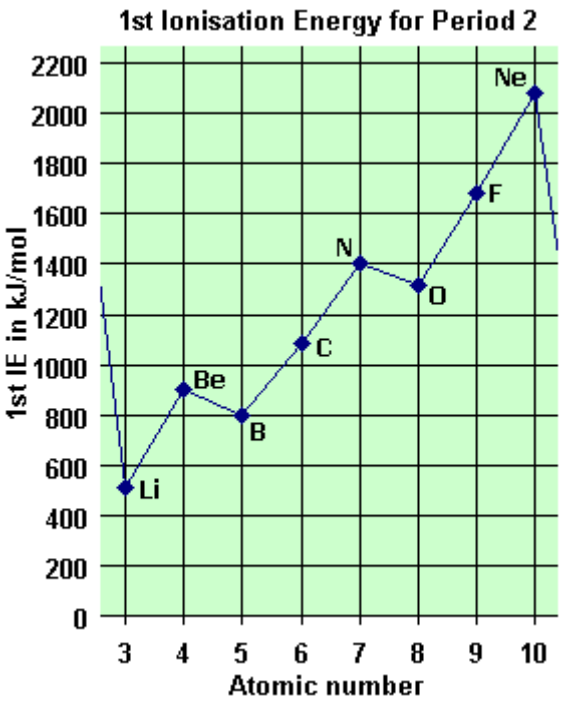


Trend:
Ionization energy generally decreases down the group in the periodic table from Lithium up to caesium

Explanation:
Down a group in the periodic table from one atom to the next one, both the nuclear charge and screening effect increase but the increase in screening effect on the electrons in the outer most shell by the electrons in the inner shells outweighs the increase in nuclear charge.
This leads to a decrease in the effective nuclear charge and hence the nuclear attraction for the outer most electrons decreases making the removal of the outer most electron require less energy. i.e. 1stionization energy generally decreases.

Variation in 1st ionisation energy across period 2 and period 3 in the periodic table:

(a) Across period 2 elements:



Trend:

Ionization energy generally increases across period 2 in the periodic table except that the one for Beryllium is unexpectedly lower than for Boron and also that for Nitrogen unexpectedly lower than for Oxygen.

Explanation:

Across period 2 in the periodic table from one atom to the next one, an electron is being added to shell number 2 and also the next atom has one more proton in its nucleus compared with the previous atom. The nuclear charge therefore increases while the screening effect of the electrons in the inner shell on the outer most electrons remains approximately constant.

These leads to an increase in the effective nuclear charge leading to an increase in the nuclear attraction for the outer most electron and hence increase in 1^{st}ionization energy.

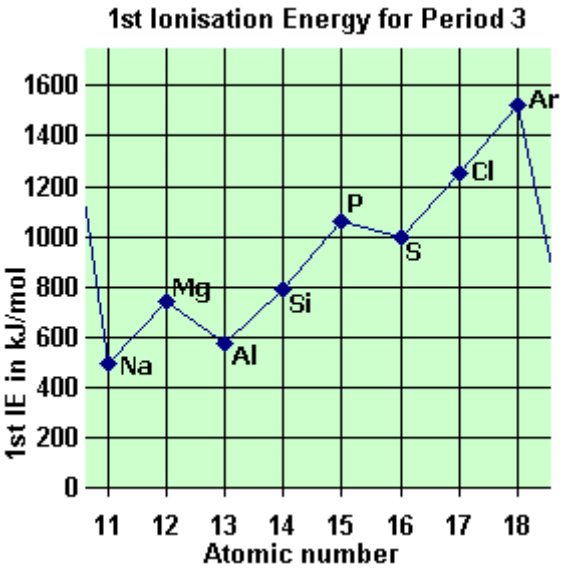
NOTE:

While explaining the trends, there are aspects that do not follow the general trend and usually need explanation. These aspects are known as **anomalies.** For example an anomaly occurs in 1st ionization energy between Beryllium and boron and its explanation is provided below

Beryllium, $1s^2 2s^2$ has a higher 1st ionization energy than Boron because the outer most 2s sub shell is full of electrons and energetically stable.
Boron, $1s^2 2s^2\ 2p^1$ loses the outer most p-electron more easily than Beryllium 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 i.e. Boron has an unstable electronic configuration.
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 thus a decrease in 1st ionization energy 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* sub-shell is building up and reaches a maximum at neon, $1s^2 2s^2 2p^6$, which has a complete stable configuration.

(b) Across period 3 elements

A similar trend as that in period 2 is observed on traversing the 3rd short period from sodium to argon.



NOTE:

In every period, noble gases have the highest 1st ionization energy. This is because noble gases have full outer most p sub shell and thus thermodynamically stable.

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

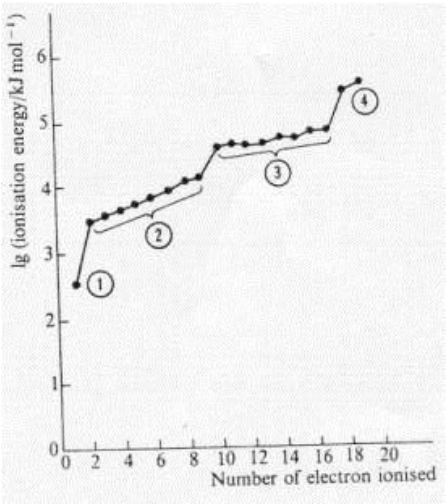
This is because Helium atom has the smallest atomic radius therefore electrons in its outer most shell is closer to the nucleus and is attracted more strongly. Also its outermost electronic configuration is thermodynamically stable.

Importance of ionization energies in understanding the chemistry of atoms of elements:

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

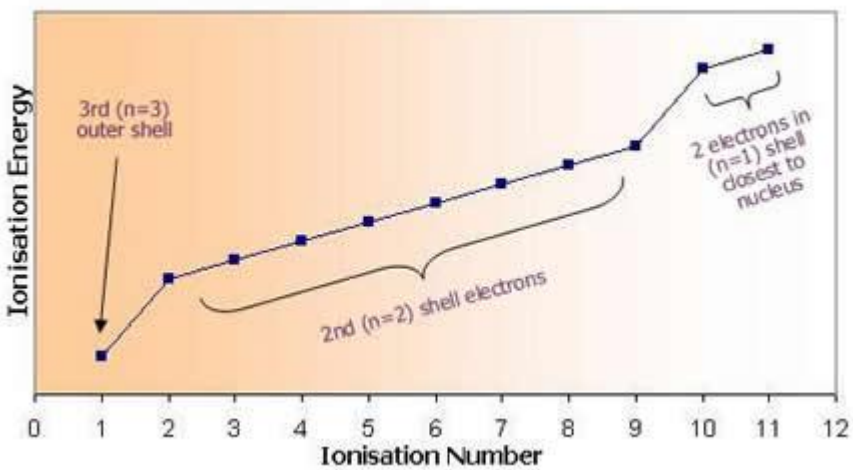
1) *Atomic number of the element*.
   This is given by the number of successive ionization energies an atom has got e.g. sodium with *11* successive ionization energies has atomic number *11*.

2) *The arrangement of electrons in the shells and distribution of energy level*.
   A plot of successive ionization energies of potassium shows distinct breaks. The arrangement starts with two electrons with fairly similar ionization energies which are both near the nucleus and difficult to remove. These are followed by 8 electrons with fairly similar variation in ionization energies. These have less ionization energies than the first two electrons. The next are eight electrons also with similar energies but are easily removed than the previous.



Potassium atom has *4* energy levels and therefore belongs to period *4* in the periodic table and also has one electron in the outer most shell, therefore it belongs to group I in the periodic table.

For a sodium atom with *11* electrons, a similar graph appears as shown in the figure below.



3) <u>*Determination of metallic or non metallic character of an atom of an element*</u>.

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

The first ionization energies of metals is all nearly below *800kj per mole* while those of non metals are all nearly above *800kj per mole*

Example:
The first three ionization energies for elements A, B, C and D are given in the table below.

Elements	*Ionization energies in kJ/mol*		
	First	*Second*	*Third*
A	*780*	*1500*	*7730*
B	*500*	*4560*	*6900*
C	*580*	*1815*	*4620*
D	*1310*	*3460*	*5300*

From the first ionization energies of the elements it can be deduced that elements B and C have typical metallic properties since their 1st ionization energies are well below *800kj/mol*
Element A with first ionization energy near *800KJmol*$^{-1}$ also would show some metallic properties.
Moving from second to third ionization energy for A there is an increase of about 5 times. This means the third electron of A comes from a different shell hence A has 2 electron on its outer most shell. A is therefore a group *2* element with a valence of *2*,

For element B, there is an increase of about *9* times from first to second ionization energies and an increase of about *1 ½times* from second to third. Therefore element B has one electron on its outer most shell and thus is a group 1 element and has a valence of, therefore would react by giving away one electron on its outermost shell.

In element C, from *1*st to *2*nd Ionization energy, there is an increase of about 3 times and from second to third by about Therefore there is similar rise in ionization energy. This implies that the three electrons in C *2 ½ times.*are from the outer most shell and C therefore has 3 electrons in its outermost shell and hence belongs to group III.

Element D with first ionization energy well over *800kjmol*$^{-1}$ is a non metal.

Testing exercise 2:

The first 8 ionization energies in KJ 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*

a) Plot a graph of ionization energies against ionization number
b) Explain the shape of the graph
c) State with reasons the group and the period in which the element belongs in the periodic table.

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

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*

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

b) Which element belongs to;

i) Group I (ii) Group II

Give a reason for your answer in each case.

ELECTRON AFFINITY:

Electron affinity is defined as the enthalpy change when one mole of gaseous atoms gains one mole of electrons to form one mole of negatively charged gaseous anions.

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

Non-metallic electronegative elements are more likely to accept one or more 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 among non metals.

The electron affinity is a measure of the attraction for the incoming electron by the nucleus of the atom gaining the electron.

The greater the attraction, the higher the electron affinity value.

First electron affinity:

First electron affinity is defined as the enthalpy change when one mole of gaseous atoms gains one mole of electrons to form one mole of univalently charged gaseous anions.

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

After the gain of an electron by a gaseous atom, the negatively charged gaseous ion formed repels any further electron to be gained.

NOTE:

First electron affinity is an exothermic process for most gaseous atoms.

Explanation:

This is because the incoming electron experiences a greater attraction from the nucleus than repulsion from the electrons already present in the atom therefore energy is released during the process

Second electron affinity

Is defined as the enthalpy change when one mole of univalently charged gaseous anions gains one mole of electrons to form one mole of divalently charged gaseous anions.

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

NOTE:

Second electron affinity is always an endothermic process.

Explanation:
This is attributed to the greater repulsive force which the electron being gained experiences from the electrons already present in the univalently charged anion; therefore work must be done to overcome the effect of this repulsion. This work involves input of heat energy.
Because of the same reason, the *3rd, 4th, 5th etc* electron affinity will have a positive enthalpy change.

FACTORS DETERMINING THE VALUE OF 1ST ELECTRON AFFINITY OF AN ATOM OF AN ELEMENT:

Electron affinity in simple terms is the measure of attraction between the incoming electron and the nucleus. The stronger the attraction, the higher the electron affinity.

The same factors affecting ionization energy also affect electron affinity but their effect is different because electron affinity is concerned with formation of negative ions while ionization energy is concerned with the formation of positive ions.
These factors are:

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius
4) Electronic configuration of the atom.
5) Penetrating power of electrons
6) Net charge on the atom or ion

Explanation:

Nuclear charge:

If the nuclear charge is high, the nuclear attraction for the incoming electron will be high. As the atom 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.
For example:

$$Na_{(g)} + e \rightarrow Na^{+}_{(g)} \qquad \Delta H = -71 KJmol^{-1}$$

$$S_{(g)} + e \rightarrow S^{-}_{(g)} \qquad \Delta H = -200 KJmol^{-1}$$

Atomic radius:

If the radius of an atom is small, the incoming electron experiences a high attraction from the nucleus of the atom. As a result 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.
For example:

$$O_{(g)} + e \rightarrow O^{-}_{(g)} \qquad \Delta H = -142 KJmol^{-1}$$

$$F_{(g)} + e \rightarrow F^{-}_{(g)} \qquad \Delta H = -348 KJmol^{-1}$$

Shielding effect of the electrons in the inner shells

If the screening effect of the electrons in the inner shells is high, then electron being gained 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 high electron affinity value.

$$Cl_{(g)} + e \rightarrow Cl^{-}_{(g)} \qquad \Delta H = -364 KJmol^{-1}$$

$$Br_{(g)} + e \rightarrow Br^{-}_{(g)} \qquad \Delta H = -342 KJmol^{-1}$$

$$I_{(g)} + e \rightarrow I^{-}_{(g)} \qquad \Delta H = -314 KJmol^{-1}$$

Electronic configuration of the outer shell:

If an electron is being added to an atom with a stable outer electronic configuration, the addition will not occur easily leading to a low electron affinity value.

Penetrating power of electrons:
In a given shell, the penetrating power of electrons towards the nucleus increases in the order f<d<p<s; therefore the s-electrons are more penetrating and experience greater nuclear attraction than those in other orbitals.
This addition of electrons in the s-orbital results in a greater electron affinity because the electron is readily attracted by the nucleus in other orbitals.

Net charge on the atom or ion:
For neutral atoms, electron affinity is exothermic.
For negatively charged ions the electron affinity is endothermic and this is because energy is required to overcome the repulsion between the negatively charged ion and the incoming electron.
The electron affinity becomes more negative with increase in the negative charge on the ion and this is because the higher the negative charge on the ion, the more energy absorbed to overcome electron repulsion to add there an electron.

Variation of electron affinity:

Generally;

Trend:
Electron affinity increases across the period while it (electron affinity) decreases down the group of the periodic table.

Explanation:
Across the period from one element to the next one, an electron is being added to the same energy level as the nuclear charge increases by 1 unit. The nuclear charge increases while the screening effect of the electrons in the inner shells on the electron to be gained is roughly constant.
The nuclear attraction for incoming electron increases leading to an increase in the1st electron affinity.

Down a group from one element to the next one, both the nuclear charge and shielding effect increase but the increase in shielding effect outweighs that due to nuclear charge as a result of the more inner shell of electrons added.
The nuclear attraction for the electron being gained decreases leading to a decrease in 1st electron affinity.

Examples:

(a) ***Across period 3 in the periodic table:***

Elements	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
1st electron affinity ($KJmol^{-1}$)	***-20***	***+67***	***-30***	***-135***	***-60***	***-200***	***-364***

Trend
Generally, electron affinity becomes more exothermic across the period as the atomic number increases.

Explanation:
Across the period from one element to the next one, an electron is being added to the same energy level as the nuclear charge increases by 1 unit. The nuclear charge increases while the screening effect of the electrons in the inner shells on the electron to be gained is roughly constant. This results into an increased effective nuclear charge thus the nuclear attraction for incoming electron increases hence more energy is released (more exothermic) in the process leading to an increase in the1st electron affinity.

Anormalies:

1. The first electron affinity of magnesium $1s^2 2s^2 2p^6 3s^2$ is endothermic because magnesium atom has a fully filled outer s-sub shell. This confers partial stability on the magnesium atom and it is less ready to accept an electron.

2. The electron affinity of phosphorous $1s^2 2s^2 2p^6 3s^2 3p^3$ is less than expected because the phosphorous atom has a half filled 3p- sub shell which is thermodynamically stable therefore it is less ready to accept an electron.

3. Silicon has an unexpectedly higher electron affinity because silicon atom has an outer shell with only two electrons in the 3p-sub shell which is thermodynamically unstable therefore it readily accepts the incoming electron.

(b) Down the Group VII elements:

Consider the first electron affinity in $Kjmol^{-1}$ for group VII elements.

Element	*1st electron affinity*
Fluorine	*-328*
Chlorine	*-349*
Bromine	*-325*
Iodine	*-295*

Trend:

The 1st electron affinity generally decreases from Chlorine to Iodine but the one for fluorine is unexpectedly lower than expected.

Explanation:

Down the group, the nuclear attraction for the incoming electron decreases.
As a result the electron being gained experiences a weaker attraction from the nucleus leading to a decrease in 1st electron affinity.
Fluorine, however, has a low value for its electron affinity, numerically less than that for chlorine.
This is due to very its small atomic radius. The 7 electrons in the outermost shell are much closer to each other that they repel each other more strongly than in the other halogens and hence the electron being added experiences a great repulsive force from the electrons already present leading to a lower than expected 1st electron affinity.

NOTE:

A similar reversal of trend happens between oxygen and sulphur in GroupVI. The first electron affinity of oxygen ($-142KJmol^{-1}$) is smaller than that of sulphur ($-200KJmol^{-1}$) for exactly the same reasons that Flourine's is smaller than Chlorine's.

ELECTRONEGATIVITY:

This is the measure of the tendency of an atom in a covalent bond to attract the bonding electrons more towards itself.

If two atoms with same electronegativity value are covalently bonded to each other, the resultant bond is 100% covalent and the resultant molecule is non polar. This happens when the bonded atoms are atoms of the same element.
Example
Cl-Cl, Br-Br, H-H, O═O etc

If two atoms with different electronegativity values are covalently bonded, the bond electrons are not shared equally. The more electronegative atom attracts the bond electrons more towards itself and in the process acquires a partial negative charge and the less electronegative atom acquires a partial positive charge. The resultant bond molecule is said to be polar and the bond has some ionic character.
Example
$H^{\delta+}-Cl^{\delta-}$, $H^{\delta+}-F^{\delta-}$, $O^{\delta-}=C^{\delta+}=O^{\delta-}$, H_2O, NH_3 etc.

FACTORS DETERMINING ELECTRONEGATIVITY VALUES:

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius

Explanation
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 high leading to a high electronegativity value.

For a low nuclear charge, the attraction by the nucleus for the bonding electrons will be low leading to a low electronegativity value.

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 leading to a high electronegativity value.

If the radius of an atom is large, the bonding electrons are far away from the nucleus and hence experience a low nuclear attraction leading to a low electronegativity value.

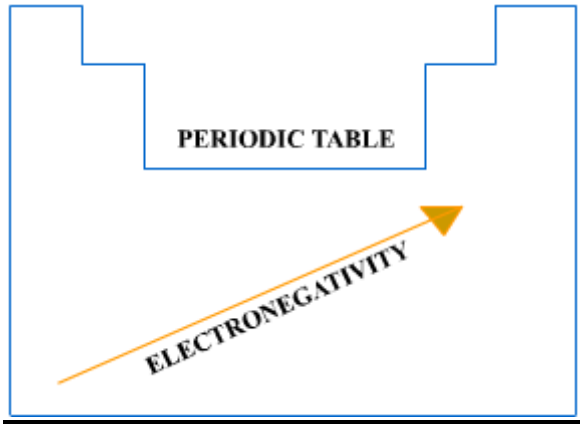
Shielding effect of the electrons in the inner shells

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 electronegativity value.

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

Variation of Electronegativity in the periodic table:

Generally:



Trend:

Electronegativity increases across the period while it increases down the group of the periodic table.

Explanation:

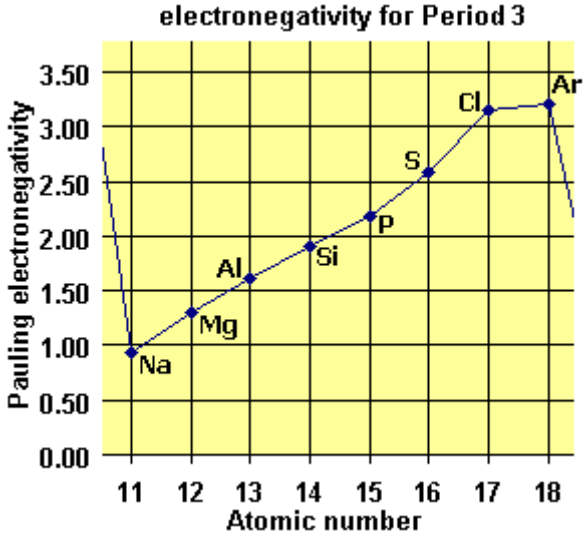
Across the period from one element to the next one, an additional electron is added to the outer most shell. As a result, the nuclear charge increases progressively while the screening effect of the inner shells of electrons remains almost unchanged therefore the effective nuclear charge increases leading to increase in the nuclear attraction for the covalent bond electrons and hence an increase in the electronegativity value.

Down any group in the periodic table from one element to the next, both nuclear charge and screening effect increase but the screening effect of the inner shells of electrons outweighs the increase in the nuclear charge due to an extra inner shell of electrons added.

The effective nuclear charge therefore decreases leading to a decrease in the nuclear attraction for the covalent bond electrons and hence a decrease in electronegativity.

Examples:

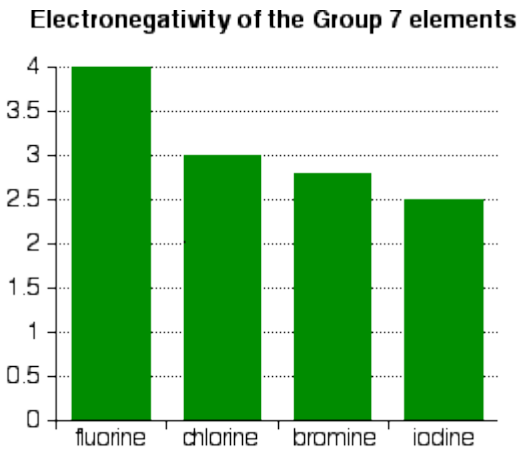
(a) Variation in electronegativity across period 3elements:



Trend:
Across the period, electronegativity increases from one element to the next one.

Explanation:
From one element to the next one, an additional electron is added to shell number 3.As a result, the nuclear charge increases progressively while the screening effect of the inner shells of electrons remains almost unchanged. Consequently, the effective nuclear charge increases leading to increase in the nuclear attraction for the covalent bond electrons and hence an increase in the electronegativity value.

Electronegativity down Group VII elements:



Down group VII elements in the periodic table from one element to the next, both nuclear charge and screening effect increase but the increase in the screening effect of the inner shells of electrons outweighs the increase in the nuclear charge due to an extra inner shell of electrons added.
The effective nuclear charge therefore decreases leading to a decrease in the nuclear attraction for the covalent bond electrons and hence a decrease in electronegativity.

ELECTROPOSITIVITY:

This is the tendency of an atom to lose one or more electrons 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 affecting electropositivity value of an atom of an element:

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius
4) Electronic configuration of the atom.

Explanation:

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. It's then not easy for the atom to lose one or more electrons leading to a decrease in electropositivity.
If the radius of an atom is large, the outer most electrons are far from the nucleus and hence experience a low nuclear attraction leading to a low electropositivity value.

Nuclear charge

If the nuclear charge is high, the electrons in the outer most shell are attracted more strongly to the nucleus as a result removing an electron from such an atom is difficult leading to a decrease in electro positivity.
For a low nuclear charge, the electrons in the outer most shell are attracted less strongly to the nucleus as a result removing an electron is relatively easy leading to an increase in electropositivity.

Shielding effect of inner shells

If the shielding effect of the electrons in the inner shells on the outer most electrons is high, the nuclear attraction for the outer most electrons is low leading to an increase in electropositivity.
For a low screening effect, the nuclear attraction for the outer most electrons increases leading to a decrease in electropositivity.

Electronic configuration of the atom

If an atom has thermodynamically stable electronic configuration, the loss of an electron will not occur easily leading to a decrease in electropositivity.
On the other hand if an atom has a less stable electronic configuration, then it easily loses an electron leading to a high electropositivity.

Variation of electropositivity in the periodic table:

Down the group:

Trend:
Electropositivity increases in moving down a group in the periodic table.

Explanation:
Down any group in the periodic table, the increase in the screening effect outweighs that due to nuclear charge due to an extra shell of electrons added from one element to the next one.
This decreases the effective nuclear charge and as a result the nuclear attraction for the outer most electrons reduces leading to an increase in electropositivity.

Across the short periods in the periodic table:

Trend:
Electropositivity decreases in moving across period 2 and 3 in the periodic table.

Explanation:
Across the period from one element to the next one, the nuclear charge increases while the screening effect of the electrons in the inner shells remains more or less unchanged because the additional electron is added to a shell with similar energy.
The effective nuclear charge therefore increases and as a result the electrons in the outer most shell are attracted more strongly by the nucleus leading to an 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 determining melting point:

1) ***Among metals:***
   The melting points of metals depend on the following factors:
   a) *The number of electrons available for metallic bonding (number of delocalized electrons per metal atom).*

The higher the number of electrons each metal atom contributes for metallic bonding, the stronger the metallic bond formed and the higher is the melting point.

b) *The atomic radius.*
If the radius of a metallic atom is small, the bonding electrons are attracted more strongly by the nucleus making the inter-atomic bond length to be shorter and stronger and thus a higher 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 inter-atomic bond becomes longer and weaker leading to a low melting point.

c) *The crystal structure of the element*.

2) Among non-metals (Molecular substances):

Melting points of non-metals depend on:

a) Molecular mass
b) Shape of molecules
c) Type of intermolecular forces of attraction.

Trends in melting point:

(a) Across period 2 elements:

Trend:

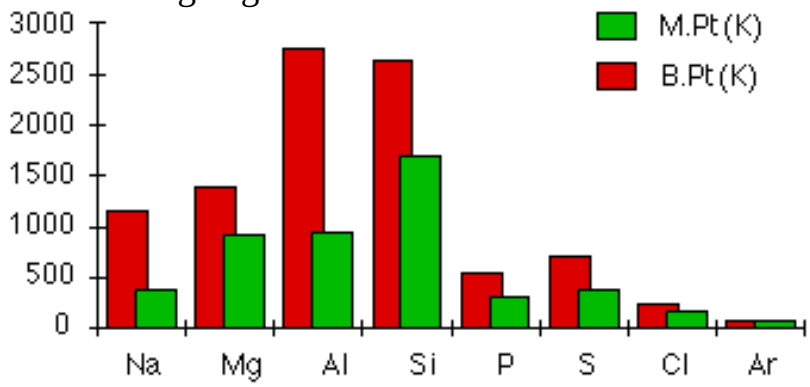
The Melting point of elements in period 2 increases from lithium to carbon and then decreases abruptly for the non metals nitrogen to neon.

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.

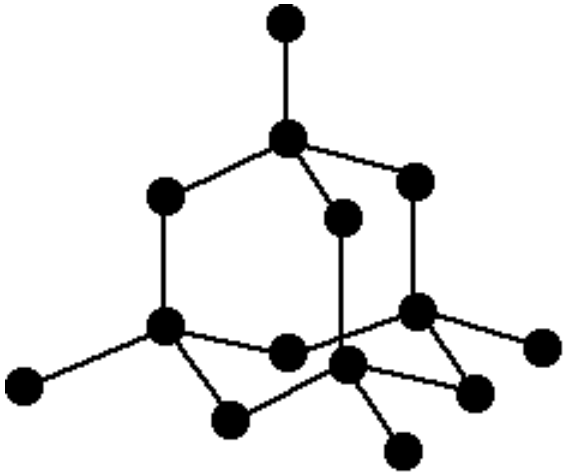
(*1* for Lithium, *2* for Beryllium,)
The greater the electrons available, the stronger the bond and the higher the melting point.
Decrease in atomic radius from Lithium to Beryllium.
The smaller the atomic radius, the closer are the bonding electrons to the nucleus and thus the shorter and stronger are the metallic bonds.
Change in the crystal structure of the elements across the period.
Lithium has a body centred cubic (b.c.c) structure which has its atoms less efficiently packed than Beryllium 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.



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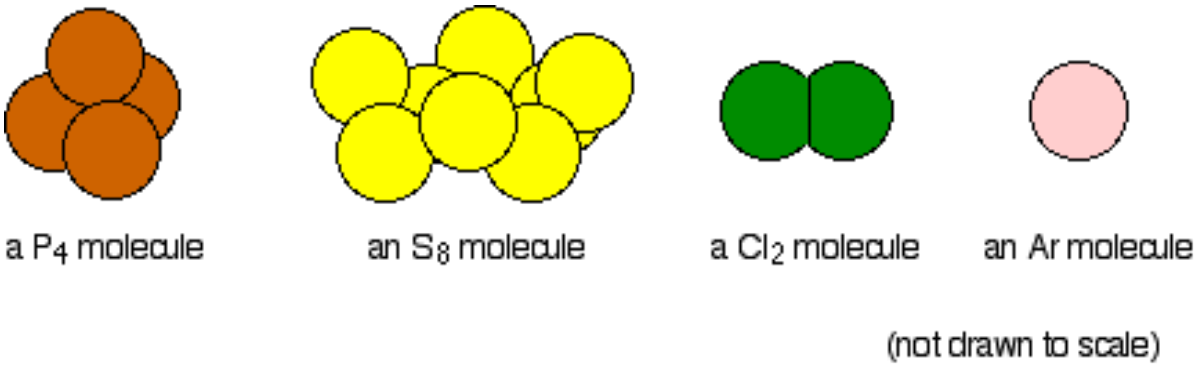
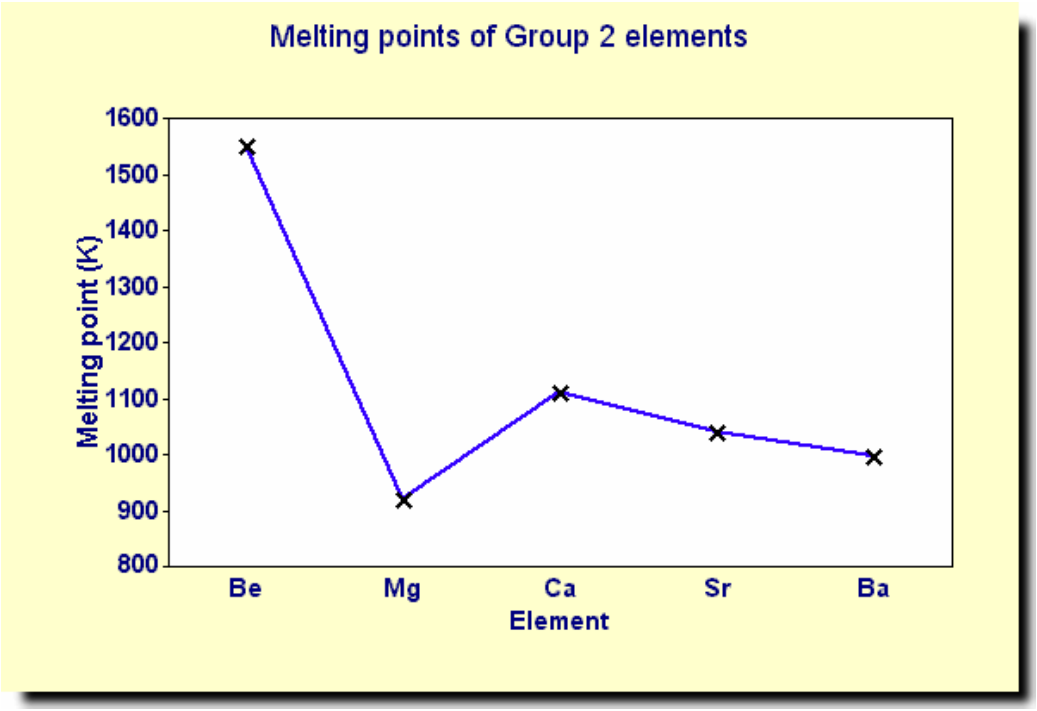
Phosphorus, sulphur, chlorine and argon have simple molecular structures held by weak van der Waals forces of attractions. Thus their melting points are much lower.
The melting and boiling points of non metals are governed entirely by the sizes of the molecules.



Phosphorus
Phosphorus contains smaller P4 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 larger S8 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 IIA elements

The melting and boiling points of its group IIA metals are higher than those of corresponding group I elements.
Graph of physical data



Explanation

Melting points generally decrease going down Group II in the periodic table.
The Group 2 elements are all metals with metallic bonding. In metallic bonding, metal cations in a metal lattice are attracted to delocalized electrons.
Therefore going down Group II:
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 beryllium.
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).

Variation in melting points among the group VII elements (halogens)

Element	*Molecular mass*	*Melting point /^{0}c*	*Boiling point /^{0}c*
Fluorine	*38*	*-220*	*-188.*
Chlorine	*71*	*-101*	*-34.*
Bromine	*160*	*-7*	*58.*

Iodine	*254*	*114*	*183.*

Trend

Both the melting and boiling points of the halogens increase from one element to the next on e down the group.

Explanation

The halogens exist as diatomic molecules i.e. F_2, Cl_2, $Br_2$and I_2.

Down the group the molecular mass increases. The increase in molecular mass leads to an increase in the magnitude of the intermolecular van der Waal's forces and hence increases in both melting and boiling points.

Example

Consider the boiling points of the hydrides of group IV elements.

Hydride	*boiling point / ^0c*
CH_4	*-161*
SiH_4	*-112*
GeH_4	*-90*
SnH_4	*-52*
PbH_4	*-12*

Trend

The boiling points of the hydrides increase down the group.

Explanation

Down the group the magnitude of the intermolecular van der waal's forces increase with increase in molecular mass.

Chapter 4

BONDING AND STRUCTURES:

Atoms take part in chemical bonding to attain stable electronic configuration of noble gases. They do so either through transfer of one or more electrons from one atom to another; a process referred to as ionic or electrovalent bonding or through sharing of electrons; a process referred to as covalent bonding.

In all bonding situations, the electrons involved are those in the outer most shell of the atoms concerned.

The following types of bonding exist;

1. Ionic or electrovalent bonding
2. Covalent bonding
3. Dative or co-ordinate bonding
4. Metallic bonding
5. Hydrogen bonding
6. Van Der Waal's forces of attraction.

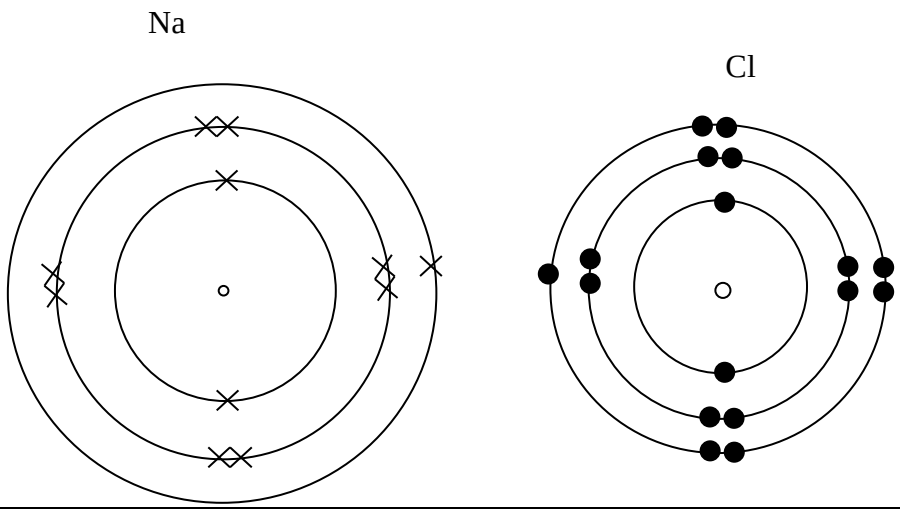
ELECTROVALENT OR IONIC BONDING:

Electrovalent or ionic bonding arises when there is transfer of one or more electrons from a metallic atom to one or more non metallic atom.

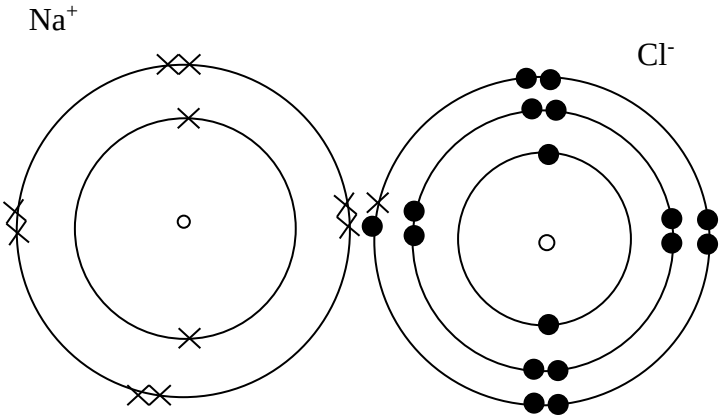
Example:

Consider the formation of sodium chloride (**NaCl**).

Before bonding:



After bonding:



Sodium atom looses the single electron in its outermost shell to form a sodium ion (***Na^+***).

A chlorine atom on the other hand gains the electron lost by the sodium atom to form a chloride ion (***Cl^-***)

The sodium and chloride ions are then attracted to each other by strong electrostatic force of attraction leading to the formation of crystalline compound with a high melting point.

Examples of other compounds formed through ionic bonding include;

- Calcium chloride; ***$CaCl_2$***
- Potassium chloride; ***KCl***
- Potassium iodide; ***KI***

- Magnesium oxide; ***MgO***
- Calcium carbonate; ***$CaCO_3$***

Properties of ionic compounds:

- They are usually crystalline solids of high melting and boiling points.
- They conduct electricity in both aqueous and molten state.
- They are usually soluble in water.

Polarization of ionic compounds:

Consider an ionic compound *AB* with A^+ and B^- as its constituent ions. The positive ion *A*+ attracts the electron clouds of the negatively charged ion B^- while at the same time repelling the positively charged nucleus of B^-. This causes distortion of the electron distribution in the B^- ions. This distortion is called polarization and leads to the covalent characteristics in the ionic compound *AB*.

The factors leading to polarization and hence covalent character in ionic compounds are summarized by the *Fajan's rule.* The rule states that an ionic compound will have appreciable covalent character if;

a) Either the cation or the anion is highly charged. A highly charged anion is highly polarizable and a highly charged cation is highly polarizing.

b) The cation has a small radius making it have a high charge density and hence a high polarizing power.

Example

Consider the melting points of sodium chloride, magnesium chloride and aluminium chloride

Chloride	*Melting point / ^0C*
NaCl	*800*
$MgCl_2$	*714*
$AlCl_3$	*180*

Trend:

Sodium chloride has the highest melting point followed by magnesium chloride and lastly by aluminium chloride.

Explanation:

The polarizing power of the cations within the chlorides increase in the order $\boldsymbol{Na^{+} < Mg^{2+} < Al^{3+}}$ with increase in cationic charge and decrease in cationic radius.

Therefore Al^{3+} is the most polarizing and $\boldsymbol{Na^{+}}$ the least polarizing. The electron clouds of the chloride ion in sodium chloride are insignificantly polarized while the electron clouds of the chloride ions in $AlCl_3$ are greatly polarized. This makes aluminium chloride predominantly covalent with a low melting point.

The sodium chloride being the most ionic has the highest melting point followed by magnesium chloride.

NOTE:
Polarization is important in explaining the diagonal relationship of elements in the periodic table.

DIAGONAL RELATIONSHIP:

This is relationship within the periodic table where by 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.

Group	*I*	*II*	*III*	*IV*	*V*
Period 2	*Li*	*Be*	*B*	*C*	*N*
Period 3	*Na*	*Mg*	*Al*	*Si*	*P*

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

Causes of diagonal relationship:

The reasons why the chemistry of the above 3 pairs of elements resemble can be summarized as follows:

- The cations in each pair have similar charge densities & similar polarizing powers.
- Similar electropositivities of the elements.
- Similar hydration energies of the cations,
- Similar electrode potentials,

<u>Resemblance between Lithium & Magnesium:</u>

The chemistry of lithium and magnesium resemble in the following ways:

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

$$6Li_{(s)} + N_{2(g)} \longrightarrow 2Li_3N_{(s)}$$

$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)}$$

2. Both react with oxygen gas when heated to form normal oxides.

$$4Li_{(s)} + O_{2(g)} \longrightarrow 2Li_2O(s)$$

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO(s)$$

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

$$4LiNO_{3\,(g)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2\,(g)} + O_{2(g)}$$

$$2Mg\,(NO_3)_{2(g)} \longrightarrow 2MgO_{(s)} + 4NO_{2\,(g)} + O_{2(g)}$$

4. Both form carbonates that decompose on heating.

$$Li_2CO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2\,(g)}$$

$$MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$$

5. Both react with carbon when heated to form ionic carbides.

$$4Li_{(s)} + C_{(s)} \longrightarrow Li_4C_{(s)}$$

$$2Mg_{(s)} + C_{(s)} \longrightarrow Mg_2C_{(s)}$$

Resemblance between Beryllium and Aluminium:

The chemistry of beryllium and aluminium resemble in the following ways;

1) Both elements are passive to concentrated nitric acid.

2) Both elements react with concentrated alkalis to form complexes. They too react with acids to form salts i.e. they are amphoteric.

Reaction with alkalis:

$$Be_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}{}_{(aq)} + H_{2(g)}$$

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

Reaction with Acids:

$$Be_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_{2(g)}$$

$$2Al_{(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$$

3) Both elements form chlorides which are partly covalent and exist as dimers in vapour phase.

4) Their oxides are amphoteric as are their hydroxides.

a) Oxides:

Reaction of oxides with alkalis:

$$BeO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}{}_{(aq)}$$

$$Al_2O_{3(s)} + 2OH^{\backslash -}_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Al(OH)_4^-{}_{(aq)}$$

Reaction of oxides with acids:

$$BeO_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_{2(g)}$$

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

b) Hydroxides:

Reaction of hydroxides with alkalis:

$$Be(OH)_{2(s)} + 2OH^-_{(aq)} \longrightarrow Be(OH)_4^{2-}{}_{(aq)}$$

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow Al(OH)^-_{4(aq)}$$

Reaction of hydroxides with acids:

$$Be(OH)_{2(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + 2H_2O_{(l)}$$

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

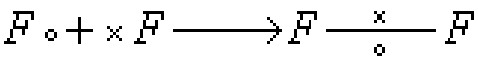
5) Both their carbides hydrolyze in water to form methane gas.

$$Be_2C_{(s)} + 4H_2O_{(l)} \longrightarrow 2Be(OH)_{2(s)} + CH_{4(g)}$$

$$Al_4C_{3(s)} + 12H_2O_{(l)} \longrightarrow 4Al(OH)_{3(s)} + 3CH_{4(g)}$$

COVALENT BONDING:

The two Fluorine atoms pair up in order to achieve the same electronic configuration as neon.



Each atom in the molecules has its outer shell electrons. The atoms in the molecules are held together by the attractive force of the two nuclei.

N.B;

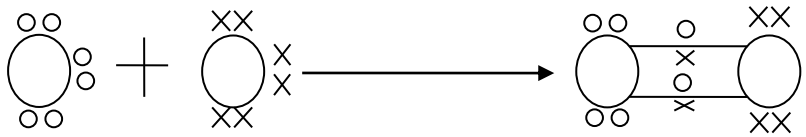
It's not only atoms of the same element which may form covalent bonds. Even atoms of different elements form covalent bonds e.g.

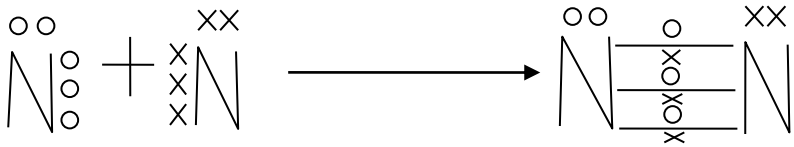
Consider the formation of hydrogen chloride.

Some atoms achieve the noble gas electronic structure by forming double or triple bonds. e.g;

Consider the formation of oxygen and nitrogen molecules.

OXYGEN

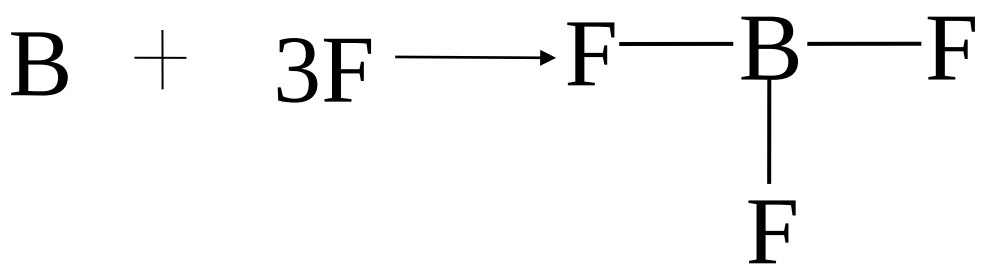




Note

Although atoms share electrons in an attempt to attain noble gas electronic configuration, they are not always successful e.g.

Consider the formation of Boron trifluoride.



Note

In BF_3 each of the fluorine atoms has attained a stable configuration of Neon but Boron has only six electrons in its outer most shell

Properties of covalent compounds:

- They consists of molecules
- They have low melting and boiling points.
- They are usually insoluble in water but soluble in non polar solvents like tetra chloromethane (CCl_4), carbon disulphide(CS_2), and benzene (C_6H_6) etc
- They are poor conductors of electricity in molten state.

Polarization of covalent bonds:

Polarization of ions in some ionic compounds leads to a degree of covalent character being developed and so it would also seem feasible that polarization of covalent bonds should give them some ionic character.

Polarization of covalent bonds occurs due to atoms having different electronegativities. If two atoms of the same element are covalently bonded, the electrons in the bond will be equally shared between them and the resultant bond is 100% covalent.

However, if the two bonded atoms are different, the bond electrons will be displaced towards the atom with the higher electronegativity and the bond is said to be polarized and will have some ionic character. It is apparent that bonds between atoms with a large difference in electronegativity will be highly polarized i.e. have a considerable ionic character.

NOTE:

There are few molecules that form pure covalent bonds. Even formation of pure ionic compounds is extreme cases. Most compounds have intermediate type of bond i.e. partially ionic and partially covalent but with one character dominating.

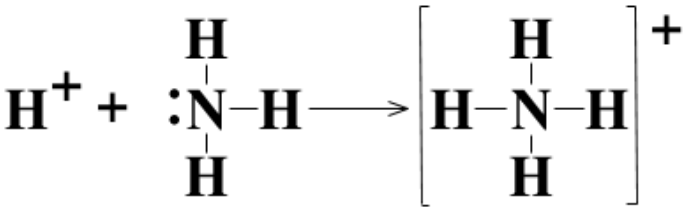
COORDINATE (DATIVE) BONDING:

This is a special type of covalent bonding in which the two electrons being shared in the bond come from only one of the participating atoms (ions). The 2nd atom (ion) only provides space to accommodate the 2 electrons. Although the mode of formation is different, once formed, a coordinate bond is the same as any covalent bond.

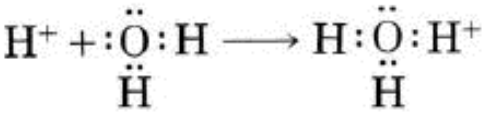
Coordinate bond is sometimes indicated by an arrow to show that they have been formed differently from covalent bonds. The arrow points away from the donor towards the recipient.

Example:

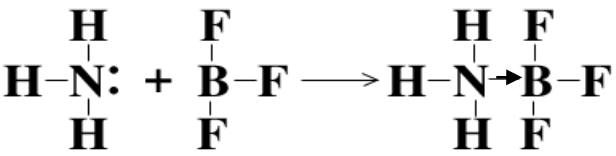
I. The formation of ammonium ion from ammonia and hydrogen ion



II. The formation of hydroxonium ion from water and hydrogen ion.



III. Consider the reaction between BF_3 and NH_3



Question

The carbon-chlorine bonds in tetrachloromethane molecule are polar and yet tetrachloromethane molecule as a whole is non polar. Explain.

Answer

Because chlorine is more electronegative than carbon, the electrons in the carbon-chlorine bonds in CCl_4 areattracted more towards the chlorine atoms.

The chlorine atoms develop partial negative charges and the carbon atom partial positive charge i.e. the carbon-chlorine bonds are polar. But because the 4 bonds are in opposite directions and are all equal, the polar effect cancel each other and overall CCl_4 is non polar.

Metallic bonding

Practically metals are silverish white in colour and are bright and shiny because they reflect all frequencies of light falling on them.

Note

Light absorption and reflection are related to energy levels and so the deduction is that metals utilize similar energy levels.

Other common features metals have in common include low ionization energies and vacant orbitals in their outer most shells. The presence of vacant orbitals in their outer most shell is essential for metallic bonding. Metals may be regarded as consisting of ions occupying fixed positions with the valency electrons moving in orbitals around the fixed ions. The valency electrons are said to be delocalized and the conduction of electricity and heat by metals is due to these delocalized electrons. The strength of the metallic bond and hence the melting point of metals increases as the number of valency electrons increases.

Van der Waal's forces of attraction

Van der Waal's forces arise from induced fluctuating dipoles in atoms and molecules. When one atom or molecule approaches another, the electrons of one or both are temporarily displaced owing to their mutual repulsion and polarization is said to occur. The slightly positive end of one molecule attracts the slightly negative end of the neighbouring molecule. It is this attraction which is the origin of van der Waal's forces of attraction.

As the atoms/ molecules move on, their electron clouds return to normal until their next encounter.

The magnitude of the intermolecular Van der Waal's forces increase with increase in the number of electrons in the molecules which depends on molecular mass.

Note

Both the melting and boiling points of molecules depend on the magnitude of the intermolecular Van der Waal's forces.

Example 1

Variation in melting points among the group VII elements (halogens)

Element	*Molecular mass*	*Melting point /^0c*	*Boiling point /^0c*
Fluorine	*38*	*-220*	*-188.*
Chlorine	*71*	*-101*	*-34.*
Bromine	*160*	*-7*	*58.*
Iodine	*254*	*114*	*183.*

Trend

Both the melting and boiling points of the halogens increase from one element to the next one down the group.

Explanation

The halogens exist as diatomic molecules i.e. F_2, Cl_2, $Br_2$and I_2.

Down the group the molecular mass increases. The increase in molecular mass leads to an increase in the magnitude of the intermolecular van der waal's forces and hence increases in both melting and boiling points.

Example 2

Consider the boiling points of the hydrides of group IV elements.

Hydride	*boiling point / ^0c*
CH_4	*-161*
SiH_4	*-112*
GeH_4	*-90*
SnH_4	*-52*

PbH_4	-12

Trend

The boiling points of the hydrides increase down the group.

Explanation

Down the group the magnitude of the intermolecular Van der Waal's forces increase with increase in molecular mass.

Hydrogen Bonding

This is a dipole –dipole attraction between a hydrogen atom bonded to an electronegative atom and a second electronegative atom having a lone pair of electrons. The atoms of the following elements are electronegative;

- Fluorine is the most electronegative element.
- Oxygen is the 2nd most electronegative after fluorine.
- Chlorine
- Bromine
- Iodine
- Nitrogen

For intermolecular hydrogen bonding to exist, at least one hydrogen atom within the molecule being considered must be directly bonded to an electronegative atom. The following molecules therefore exhibit intermolecular hydrogen bonding.

H_2O, NH_3, CH_3CH_2OH, HCl, HBr, HI, CH_3NH_2, CH_3COOH *etc*

Note

Hydrogen bonds are infact similar to Van der Waal's forces except that they are much stronger than Van der Waal's forces in molecules of comparable molecular masses.

Evidence for the existence of hydrogen bonding

Example 1

Consider the hydrides of group VI elements

Hydride	*Molecular mass/g*	*boiling point/ ^0c*
H_2O	*18*	*100*
H_2S	*34*	*-60*
H_2Se	*81*	*-41*
H_2Te	*130*	*-2*
H2Po	*211*	

Trend

Except for water, the boiling point increases down the group with increase in molecular mass of the hydride.

Explanation

Save for water, the boiling point of the hydrides increase down the group with increase in the magnitude of the intermolecular Van der Waal's forces with increasing molecular mass.

Note

Water with the lowest molecular mass has the highest boiling point due to the very strong intermolecular hydrogen bonds between its molecules.

Example 2

Consider the hydrides of group VII

Hydride	*Boiling point /^{0}c*
HF	*20*
HCl	*-85*
HBr	*-67*
HI	*-35*

Trend

Except for HF, the boiling point increases down the group with increase in molecular mass of the hydrides.

Explanation

From hydrogen chloride through hydrogen bromide to hydrogen iodide, the boiling point increases down the group due to the increase in magnitude of the intermolecular van der waal's forces with increasing molecular mass of the hydrides.

Note

In hydrogen fluoride, the intermolecular hydrogen bonds are quite strong because fluorine is highly electronegative. This explains the very high boiling point of hydrogen fluoride in comparison to the other hydrides in the group.

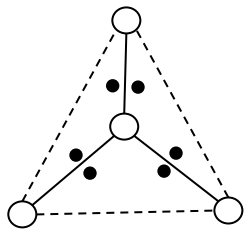
Shapes of Molecules and Ions;

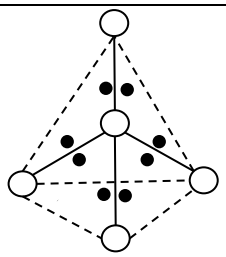
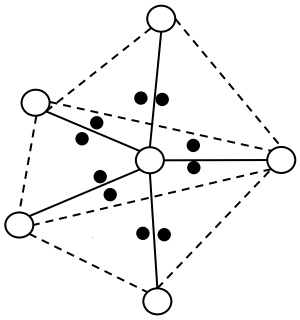
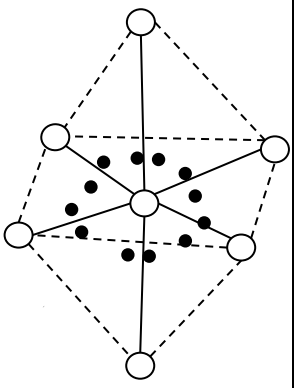
The shape of a given molecule or ion is determined by number of electron pairs present in the outermost shell of the central atom within the molecule or ion.

These electron pairs repel one another one and so they try to get as apart as possible.

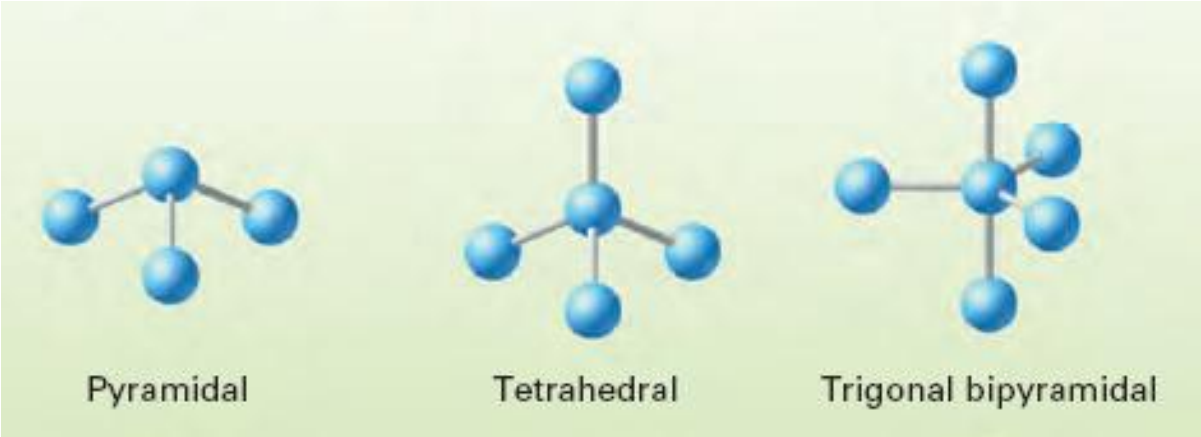
- In the outer shell of the central atom there could be;
  - Only bond pairs of electrons e.g. in methane; CCl_4
  - Bond and lone pairs of electrons e.g. in NH_3, H_2O, H_2Setc
- A lone pair of electrons is closer to the nucleus of the central atom than the bond pairs and therefore the repulsion of the lone pairs of electrons have for the bond pairs is so strong i.e. the bond pairs are pushed closer to each other by a lone pair.
- Multiple (double or triple) bonds occupy only one position in space and so from the point of view of molecular shapes act as a single bond

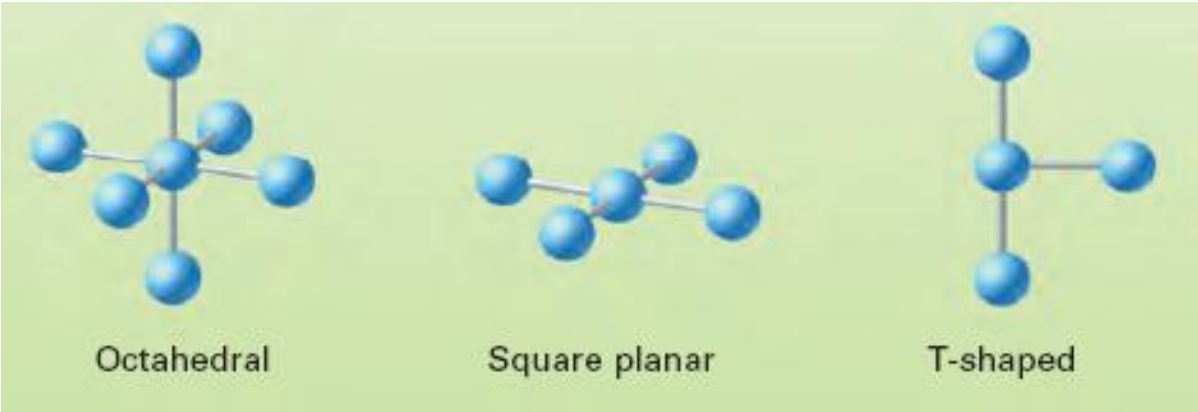
Table 1: Structure of simple molecules

Number of bond pairs on the outer most shell of the central atom	*Structure*	*shape*	*Bond angles*	*Example*
2 (All bond Pairs)		*Linear*	180^0	CO_2 , HCN
3 (All bond pairs)		*Trigonal Planar*	120^0	BF_3 , BCl_3

4 (All bond pairs)		*Tetrahedral*	*109.5 0*	*CCl_4, CH_4*
5 (All bond pairs)		*Trigonalbipyramidal*	*120^0, 90^0*	*PCl_5*
6 (all bond pairs)		*Octahedral*	*90^0*	*$[Al(H_2O)_6]^{3+}$ $[Fe(H_2O)_6]^{3+}$*

The above structures look like the figures shown below in three dimensions.





Example 1

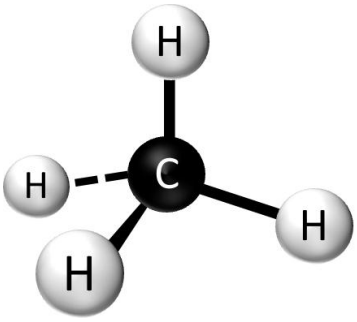
CH_4

Central atom is C. Its atomic number is 6 (2:4)

The central carbon atom contributes a total of 4 electrons. (4×1)

The 4 hydrogen atoms contribute a total of 4 electrons.

Total number of electrons is 8 electrons (4 pairs, all bond pairs.)



The H-C-H bond angle is 109.5^0

Note.

Other molecules that adopt tetrahedral shape include CCl_4, $SiCl_4$ *e.t.c*

Example 2

PCl_5

central atom is P

Its atomic number is 15 (2:8:5)

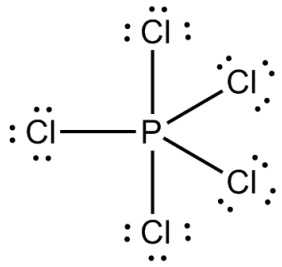
P contributes 5 electrons.

The 5 chlorine atoms contribute a total of 5×1 =5 electrons.

The total of electrons is 10 electrons = (5 pairs, all bond pairs)

Structure: shape:

Trigonalbipyramidal



Molecules having both lone and bond pairs of electrons.

Example 1

NH_3

The central atom is nitrogen

Its atomic number is 7 (2:5)

Nitrogen atom contributes 5 electrons.

The 3 hydrogen atoms contribute (3×1) 3 electrons.

Total = 8 electrons (4 pairs; 3 bond pairs and1 lone pair).

Exercise

Draw the structure and name the shape of the above molecule

Note.

In NH_3there are 4 electron pairs in the outer shell of the central nitrogen atom. Given 4 electron pairs, the angle between any two bonds in a molecule is expected to be 109.5^0 but in ammonia, the H-N-H bond angle is only $107^{0.}$

Explanation.

Of the 4 electron pairs present in the outermost shell of the central nitrogen atom in ammonia, 1 pair is alone pair and the other 3 are bond pairs.

The lone pair being closer to the nitrogen nucleus repels the 3 bond pairs more strongly than the bond pairs repel themselves and hence the H-N-H angle reduces to 107^0.

Example 2

H_2O

Central atom is oxygen.

Its atomic number is 8 (2:6 or $1S^2 2S^2 2P^4$)

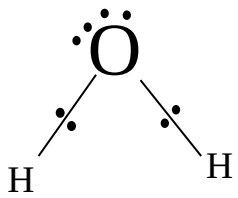
Oxygen contributes 6 electrons

The 2 Hydrogen atoms contribute a total of 2 electrons.

Total number of electrons = 8 electrons (4 pairs; 2 lone and 2 bond pairs).

Structure.Shape

V- Shaped or angular or bent



Note

The H-N-H bond angle is 104.5^0 instead of the expected 109.5^0

Explanation.

The 2 lone pairs push the 2 bond pairs more strongly than the bond pairs push themselves.

The repulsion between the bond pairs of electrons will therefore be minimal when the H-N-H bond angle is 104.5^0

Example 3

NH_4^+ ($NH_3 + H^+ \longrightarrow NH_4^+$)

Central atom is N 7 (2:5)

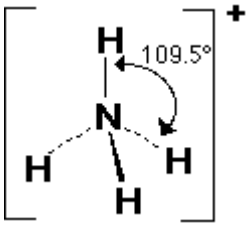
N atom contributes 5 electrons

3 hydrogen atoms contributes 3 ×1= 3 electrons

H^+ contributes 0 electrons

Total number of electrons = 8 electrons (4 pairs; all bond pairs).

Structure: *shape:*



Tetrahedral

Example 5

PCl_3

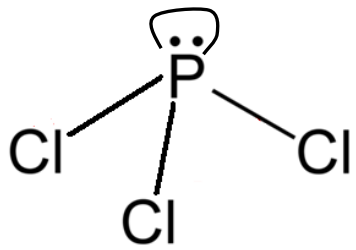
Central atom is phosphorous. 15 (2:8:5)

Phosphorus contributes 5 electrons

3 Chlorine atoms contribute a total of 3 ×1 =3 electrons

Total number of electrons =8 electrons (4pairs; 3bond and1lone pair)

Structureshape Trigonal pyramidal



Example 6

CO_2

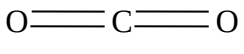
Central atom is C, 6 (2:4) ($1S^2 2S^2 2P^2$)

Carbon contributes 4 electrons.

The two 0_2 atoms contribute (2×2) = 4 electrons.

Total number of electrons =8 electrons (4 pairs.)

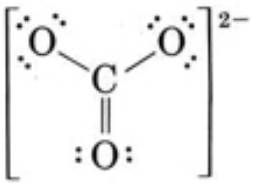
Structure *shape: Linear*



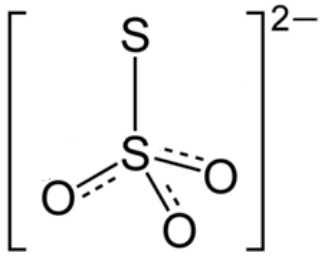
Shapes of some common ions.

a) *CO_3^{2-}(Trigonal Planar)*

Structure:

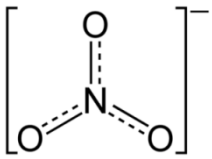


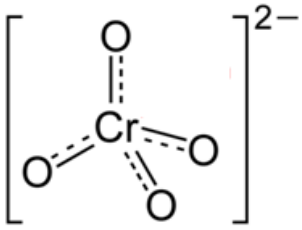
c) *$S_2O_4^{2-}$(Tetrahedral)*



d) *NO_3^-(Trigonal Planar)*

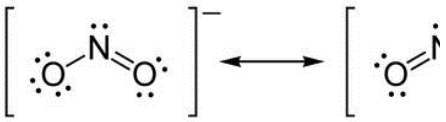
Structure:





e) NO_2^-*(V – shape)*

Structure:

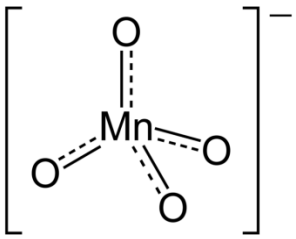


f) CrO_4^{2-}

Structure

g) MnO_4^-

Structure,



Question

Both H_2O and H_2S molecules adopt v- shaped but the bond angle in H_2O is greater than that in H_2S.

Answer

Oxygen atom being more electronegative than sulphur pulls the bond electrons more towards its self and in the process drawing the bond pairs of electrons nearer. This increases the repulsion between the bond pairs and to reduce the repulsion to a minimum, the bond angle increases.

In H_2O therefore the two bond electrons repel each other more strongly than those in H_2S. The greater the repulsion between the bonds pairs the greater the bond angles.

Chapter 4

GROUP IA ELEMENTS (ALKALI METALS) and GROUP IIA ELEMENTS (ALKALINE EARTH METALS)

Physical properties of group IA elements:

Element	*Atomic no*	*Outer elect conf*	*1st I.E /kjmol^{-1}*	*Atomic radius / ^{0}A*	*Melting pt /^{0}c*
Lithium	*3*	*-2s^1*	*520*	*0.15*	*181*
Sodium	*11*	*-3s^1*	*500*	*0.19*	*98*
Potassium	*19*	*-4s^1*	*420*	*0.23*	*63*
Rubidium	*37*	*-5s^1*	*400*	*0.24*	*39*
Caesium	*55*	*-6s^1*	*380*	*0.60*	*29*

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 (where *n= 2, 3, 4, 5,6).*

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

They have the largest atomic radii and lowest ionization energies than any element within the period.

They are highly electropositive and the most reactive metals.

Physical properties of Group II elements:

Element	*Atomic no*	*Outer elect conf*	*Ionic radius/^{0}A*	*1st ionization energy/kjmol^{-1}*
Beryllium	*4*	*-2s^2*	*0.31*	*899*
Magnesium	*12*	*-3s^2*	*0.65*	*738*
Calcium	*20*	*-4s^2*	*0.97*	*589*
Strontium	*38*	*-5s^2*	*1.13*	*549*
Barium	*56*	*-6s^2*	*1.35*	*502*

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 (n= *2, 3, 4, 5, 6*)

They have smaller atomic radii than corresponding group I metals.

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

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

They are less electropositive, less reactive and form less ionic compounds than group I.

CHEMICAL PROPERTIES OF GROUP I AND II ELEMENTS

1. *Reaction with Hydrogen*.

The more electropositive metals of group I & II react with hydrogen when heated to form ionic hydride except Beryllium and Magnesium which form covalent hydride.

$$2Na_{(s)} + H_{2(g)} \longrightarrow 2NaH_{(s)}$$

$$Ca_{(s)} + H_{2(g)} \longrightarrow CaH_{2(s)}$$

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

$$NaH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$$

2. *Reaction with Water*.

All group I 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

A group I element loses one electron while a group II element loses two electrons. Therefore less energy is required to remove one electron than two from the outer most shell and as such group I metals react faster with water than their neighbouring metals of group II.

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

$$2X_{(s)} + H_2O_{(l)} \longrightarrow 2XOH_{(aq)} + H_{2(g)}. \qquad X = Li, Na, K, Rb, Cs.$$

Beryllium does not react with water.

Magnesium reacts with steam to form Magnesium oxide (white solid) and hydrogen gas.

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}.$$

Calcium, Strontium, and Barium react with increasing vigour with cold water forming corresponding hydroxide and hydrogen gas.

$$X_{(s)} + 2H_2O_{(l)} \longrightarrow X(OH)_{2(aq)} + H_{2(g)} \qquad X= Ca, Sr, \& Ba.$$

Note

Solubility of group II hydroxides in water

.

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*

Trend

The solubility of group II hydroxides increases down the group.

Explanation

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

But the decrease in lattice energy of the hydroxides is more rapid than the decrease in hydration energy.

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

3. *Reaction with acids.*

a) Dilute and concentrated hydrochloric acid

Group II metals react with hydrochloric acid forming corresponding salt and hydrogen gas.

$M_{(s)} + 2H^+_{(aq)} \longrightarrow M^{2+}_{(aq)} + H_{2(g)}$ **(M= Be, Mg, Ca, Sr, Ba)**

b) Dilute sulphuric acid.

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

$Be_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_{2(g)}$

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

$Mg_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}(aq) + H_{2(g)}$

Calcium, Strontium & Barium react to form a sparingly soluble sulphate which renders the reaction passive.

c) Reaction with 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.

$M_{(s)} + 2H_2SO_{4(l)} \longrightarrow MSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$ **(M = Mg, Ca, Sr, Ba.)**

d) Reaction with nitric acid.

Beryllium does not react with nitric acid at all conditions.

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

$Mg_{(s)} + 2HNO_{3(aq)} \longrightarrow Mg(NO_3)_{2(aq)} + H_{2(g)}$

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

$Mg_{(s)} + 4HNO_{3(aq)} \longrightarrow Mg(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

Calcium, Strontium & Barium react with nitric acid to form salt, nitrogen dioxide and water.

$$Ba_{(s)} + 4HNO_{3(aq)} \longrightarrow Ba(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

4. *Reaction with Oxygen*.

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

a) *Normal oxide (O^{2-})*

b) *Peroxide (O_2^{2-})*

c) *Superoxide (O_2^{-})*

All group I metals form normal oxide with oxygen.

$$4M_{(s)} + O_{2(g)} \longrightarrow 2M_2O_{(s)} \quad (M= Li, Na, K, Rb, Cs.)$$

Elements sodium to caesium in addition form peroxides.

$$2M_{(s)} + O_{2(g)} \longrightarrow M_2O_{2(s)} \quad (M= Na, K, Rb, Cs.)$$

Elements K to Cs in addition form superoxide.

$$M_{(s)} + O_{2(g)} \longrightarrow MO_{2(s)} \quad (M= K, Rb, Cs)$$

Note

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

All group II metals when heated in air form normal oxides.

$$2M_{(s)} + O_{2(g)} \longrightarrow 2MO_{(s)} \quad (M= Be, Mg, Ca, Sr, Ba)$$

The more electropositive metals form peroxides e.g Strontium & Barium.

$$M_{(s)} + O_{2(g)} \longrightarrow MO_{2(s)} \quad (M = Sr, Ba)$$

Note:

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.

$$BeO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}{}_{(aq)}$$

$$BeO_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_{2(g)}$$

The other oxides are ionic and basic in nature.

5. *Reaction with halogens*.

All the metals of group I & II combine directly under heat to form chlorides.

$$2Li_{(s)} + Cl_{2(g)} \longrightarrow 2LiCl_{(s)}$$

$$Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$$

COMPOUNDS OF GROUP I AND II ELEMENTS

Compounds of group II elements are less ionic than their corresponding group I compounds.

Explanation

The cations of group II have smaller ionic radius than corresponding group I.

Also group II cations are doubly charged while those of group I are singly charged.

Therefore cations of group II have higher charge density and more polarizing power than corresponding group I cations. As such compounds of group II are less ionic than corresponding group I compound. e.g. Magnesium chloride is less ionic than Sodium chloride.

Solubility of ionic salts in water

Solubility of an ionic salt in water is determined by two energy terms:

a) Lattice energy of the salt.

b) Hydration (solvation) energies of the constituent ions of the salt.

Lattice energy:

This is the energy required to decompose 1 mole of an ionic salt into its constituent gaseous ions.

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

Or

It is the amount of energy given out when 1 mole of an ionic salt is formed from its constituent gaseous ions.

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

Hydration energy:

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

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

Hydration energy has a negative ΔH sign because it involves release of heat energy.

Example

1) Each ion has its own hydration energy.

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

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

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

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

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

3) Water is a suitable solvent for dissolving ionic salts because:

   a) it is a polar solvent,

   b) has a high dielectric constant.

   c) has a large dipole moment, so that ion-dipole interaction is high.

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

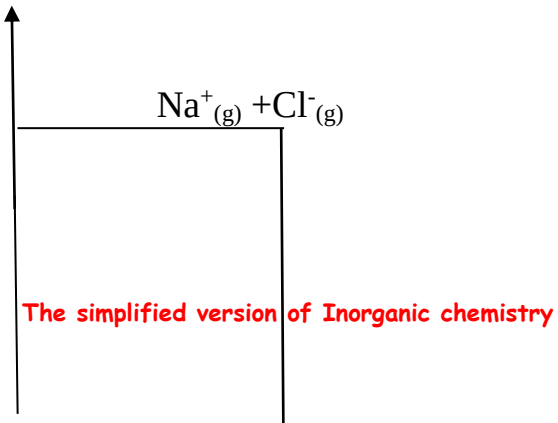
If the hydration energy is less than the lattice energy then the substance dissolves endothermically.

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

Enthalpy of solution:

This is defined as the heat change when 1 mole of an ionic salt is completely hydrated in water.

$NaCl_{(s)} + aq \longrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$ Δ **H = enthalpy of solution**



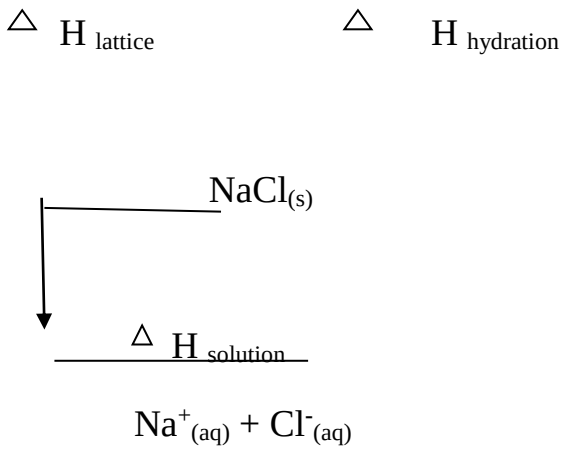


Figure shows Born-Haber cycle for solubility of sodium chloride in water.

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

<u>Note</u>:

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

<u>Exercise 1</u>

The lattice and hydration energies of $MgCl_2$ are -2644 $kJmol^{-1}$ and -2653 $kJmol^{-1}$ respectively.

a) Draw an energy diagram (Born-Haber cycle) for the solubility of $MgCl_2$ in water and indicate the energy changes that occur.

b) Calculate the enthalpy of solution of the salt.

<u>Exercise 2</u>

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

b) The enthalpy of solution and lattice energy of potassium iodide are +21$kJmol^{-1}$ and -642$kJmol^{-1}$ respectively. Calculate the hydration energy for potassium iodide.

Factors determining the lattice energy of a given ionic salt:

a) Ionic charge (charge on the ion)

b) Ionic radius

Explanation

Ionic charge

Lattice energy is directly proportional to the ionic charge.

If ionic charge is high, then the electrostatic forces of attraction between the oppositely charged ions are stronger leading to high lattice energy.

If ionic charge is small, the electrostatic forces of attraction between the oppositely charged ions are weaker leading to low lattice energy.

Ionic radius

Lattice energy is inversely proportional to ionic radius.

If ionic radius is large, the electrostatic forces of attraction between the oppositely charged ions are weaker leading to low lattice energy.

On the other hand if the ionic radius is small, the electrostatic force of attraction between the oppositely charged ions is greater leading to high lattice energy.

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

Explanation

The cations of group II have smaller ionic radius than corresponding group I.

Group II cations are doubly charged while those of group I are singly charged.

Therefore the lattice energy of group II salts are much higher than those of corresponding group I salts.

The higher lattice energy of group II salts makes them less soluble than their corresponding group I salts.

Sulphates of group I & II elements:

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

Sulphates of group II are white solids and sparingly soluble in water.

Solubility of group II sulphates in water

.

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*

Trend

The solubility of the sulphates decrease down the group

Explanation

Down the group, the radius of the cations increases 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.

Note

Solubility of the nitrates carbonates and chromates follow a trend similar to those of the sulphates.

Carbonates of group I & II elements:

The carbonates of group I metals are white solids; readily dissolve in water and are unaffected by heat except lithium carbonate which decomposes on heating.

$$Li_2CO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2\,(g)}$$

Explanation

Li^+ ion has a very small radius giving it a high charge density and a high polarizing power. As such the Li^+ ion is capable of forming a stable compound with an oxide ion.

However, as the group is descended the radii of the cations increase and their charged densities decrease. Thus they cannot 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 carbon dioxide gas.

$$MCO_{3(s)} \longrightarrow MO_{(s)} + CO_{2(g)} \quad (M = Be, Mg, Ca, Sr, Ba)$$

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 charge densities of the metal cations progressively decrease due to increase in cationic radius.

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

Nitrates of group I & II elements.

Group I nitrates (except lithium nitrate) decompose on heating forming nitrites and oxygen.

$$2MNO_{3(s)} \longrightarrow 2MNO_{2(s)} + O_{2(g)} \quad (M = Na, K, Rb, Cs)$$

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

$$4LiNO_{3(s)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

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-}) approaches the Li^+ ion more closely and 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 relatively smaller nitrites. The decrease from nitrate to nitrite stabilizes the compound.

Complex formation by group II cations

Complex ion formation is favoured by:

a) Presence of suitable empty orbitals on the cations to accommodate the lone pairs of electrons donated by ligands.

a) Small cationic radius.

b) High cationic charge.

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 decreases with decrease in cationic charge density.

Beryllium cation forms complex easily due to its very small ionic radius & high charge density e.g. $Be(OH)_4^{2-}$, $Be(H_2O)_4^{2+}$

Reactions in which Beryllium resembles other group II elements include:

a) Burns in air to form normal oxide.

b) Reacts with chlorine gas when heated to form chloride.

c) Reacts with dilute hydrochloric acid liberating hydrogen gas.

Reactions in which Beryllium differs from other group II metals include:

a) Beryllium reacts with conc. alkalis but other group II elements do not.

b) Beryllium oxide is amphoteric i.e. shows both basic and acidic properties but other oxides of the group II elements are basic in nature.

c) Beryllium carbide reacts with water to form methane.

d) Beryllium chloride is partly covalent and exists as dimer in vapour state. Other members form ionic chlorides.

ANALYSIS OF MAGNESIUM, CALCIUM AND BARIUM IONS IN SOLUTIONS

1) Use of sodium hydroxide solution.

Procedure

To the solution containing the unknown cation is added sodium hydroxide solution dropwise until in excess.

Observation

a) With Mg^{2+}, a white precipitate of magnesium hydroxide, insoluble in excess sodium hydroxide is observed.

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

With Ca^{2+}, a white precipitate of calcium hydroxide, insoluble in excess sodium hydroxide is formed

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

b) With Ba^{2+} a white precipitate of barium hydroxide, insoluble in excess sodium hydroxide is formed

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

2) Aqueous ammonia solution

Procedure

To the solution containing the unknown cation is added aqueous ammonia solution dropwise until in excess.

Observation

a) With Mg^{2+}, precipitate of magnesium hydroxide, insoluble in excess ammonia is observed.

b) With Ca^{2+} or Ba^{2+} ions there is no observable change.

Explanation

Aqueous ammonia being a weak base does not have hydroxide ions in sufficient concentration to exceed the solubility products of $Ca(OH)_2$ and $Ba(OH)_2$ which are quite high.

3) Use of dilute suphuric acid or any solution containing sulphate ions.

Procedure

To a few cm^3 of the solution containing the unknown cation is added dilute sulphuric acid (sodium sulphate solution or potassium sulphate can also be used).

Observation

a) There is no observable change with Mg^{2+}

b) With either Ca^{2+} or Ba^{2+} a white precipitate of either calcium sulphate or barium sulphate is formed.

Equation

$$Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow CaSO_{4(s)}.$$

$$Ba^{2+}_{(aq)} + SO4^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$$

4) Use of potassium chromate solution

Procedure

To the solution containing the unknown cation is added potassium chromate solution followed by ethanoic acid.

Observation

a) With Mg^{2+} there is no observable change.

b) With Ca^{2+} a yellow precipitate of calcium chromate soluble in ethanoic acid is formed.

$$Ca^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow CaCrO_{4(s)}$$

c) With Ba2+ a yellow precipitate of barium chromate insoluble in ethanoic acid is formed.

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

5) <u>Use of ammonium oxalate solution</u>

<u>Procedure</u>

To the solution containing the unknown cation is added ammonium oxalate solution followed by ethanoic acid.

<u>Observation</u>

a) With Mg^{2+} there is no observable change.

b) With Ca^{2+} a white precipitate of calcium oxalate insoluble in ethanoic acid is formed.

$$Ca^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \longrightarrow CaC_2O_{4(s)}$$

c) With Ba^{2+} a white precipitate of barium oxalate soluble in ethanoic acid is formed.

$$Ba^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \longrightarrow BaC_2O_{4(s)}$$

6) <u>Use of disodium hydrogen phosphate solution</u>

<u>Procedure</u>

To the solution containing the unknown cation is added little aqueous ammonia followed by ammonium chloride and then a few drops of disodium hydrogen phosphate.

<u>Observation</u>

a) With Mg^{2+} a white precipitate is formed

b) There is no observable change with Ca^{2+} and Ba^{2+} ions.

Exercise I

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

a) Calculate the empirical formula of Z.

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

c) Write the structural formula of Z.

Exercise II

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

a) Calculate the empirical formula of X.

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

c) Write the structural formula of X.

Exercise III.

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

a) Calculate the relative mass of iron chloride.

b) Determine the molecular formula of the iron chloride.

c) Write the structural formula of the iron chloride.

Exercise IV.

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

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

Exercise V.

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

a) Warm dilute sulphuric acid.

b) Warm conc. sodium hydroxide.

CHAPTER 5

GROUP (IV) ELEMENTS

Table 2: physical properties of group IV elements

Element	*Atomic no*	*Outer elect conf*	*Atomic radius /^{0}A*	*Electronegativity*
Carbon	*6*	*-$2s^2 2p^2$*	*0.077*	*2.50*
Silicon	*14*	*-$3s^2 3p^2$*	*0.177*	*1.75*
Germanium	*32*	*-$4s^2 4p^2$*	*0.122*	*2.00*
Tin	*50*	*-$5s^2 5p^2$*	*0.140*	*1.70*
Lead	*82*	*-$6s^2 6p^2$*	*0.154*	*1.55*

Physical properties of group (IV) elements

All group (IV) elements have four electrons in their outermost shell with a general outer configuration of ns^2np^2 (where *n= 2, 3, 4, 5, 6*).

Metallic character increases down the group as the radius of the atoms become larger. Carbon and Silicon are non metals, Germanium is a metalloid i.e. it exhibits properties characteristic of metals and non metals while Tin & Lead are weak metals.eg they form amphoteric oxides

All elements show 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 (II) compouds.eg

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

$$PbCl_{4\,(l)} \longrightarrow PbCl_{2(s)} + Cl_{2\,(g)}$$

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.

Note:

Carbon, however, being the most electronegative group (IV) element 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 exhibits a unique property called *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 forms limitless hydrides i.e. alkanes, alkenes, alkynes etc due to its catenation ability. 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 in descending 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) becomes 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.

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

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

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

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

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

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

<u>Note</u>

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

2) <u>Reaction with Oxygen (air)</u>.

a) Carbon.

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

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

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

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

$Si_{(s)} + O_{2\,(g)} \longrightarrow SiO_{2(s)}$

$Ge_{(s)} + O_{2(g)} \longrightarrow GeO_{2(s)}$

$Sn_{(s)} + O_{2(g)} \longrightarrow SnO_{2(s)}$

$2Pb_{(s)} + O_{2(g)} \longrightarrow 2PbO_{(s)}$

3) <u>Reaction with acids</u>

a) Carbon is attacked by all oxidizing acids e.g hot concentrated sulphuric acid and hot concentrated nitric acids.

$C_{(s)} + 4HNO_{3\,(aq)} \longrightarrow CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$

$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$

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

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

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

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

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

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

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.

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

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

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

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

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

4) <u>Reaction with Alkalis</u>

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

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

Germanium dissolves in conc. Alkalis to form hexahydroxogermanate (iv)

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

<u>Ionically</u>

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

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

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

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

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.

<u>The oxides of group (IV)</u>

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 shows both acidic and basic properties is said to be <u>amphoteric</u>.

<u>Monoxides</u>

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.

$NaOH_{(aq)} + CO_{(g)} \longrightarrow HCOONa_{(aq)}$

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 germinate(II), stannate(II) and plumbate(II) complex ions.

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

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

Similar reactions are undergone by Germanium monoxide & lead (ii) oxide

Alternatively:

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

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

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

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

They all react with concentrated hydrochloric acid.

$MO_{(s)} + HCl_{(aq)} \longrightarrow MCl_{2(aq)} + H_2O_{(l)}$

where M can be Ge or Sn.

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.

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

$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$

$Ge_{(s)} + O_{2(g)} \longrightarrow GeO_{2(s)}$

$Sn_{(s)} + O_{2(g)} \longrightarrow SnO_{2(s)}$

$2\,Pb_{(s)} + O_{2(g)} \longrightarrow 2PbO_{(s)}$

Note

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

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

Brown solid

With warm conc. hydrochloric acid, red lead (trilead tetra oxide) reacts according to the equation:

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

Yellow solution

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

The structure of carbon dioxide

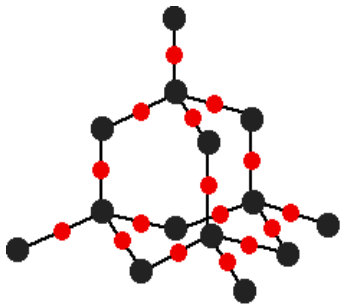
There is an enormous difference between the physical properties of carbon dioxide and silicon dioxide (also known as silicon (IV) oxide or silica).

Carbon dioxide is a gas whereas silicon dioxide is a hard high-melting solid.

The other dioxides in Group 4 are also solids. The fact that carbon dioxide is a gas means that it must consist of simple or discrete molecules held by weak Van der Waals forces of attraction. These forces are not strong enough to bind the carbon dioxide molecules into solid.

Carbon dioxide has a linear structure because the double bonds repel each other strongly to give a structure with bond angle 180 degrees as there are no lone pairs available

The structure of silicon dioxide



This is based on a diamond structure with each of the silicon atoms being bridged to its other four neighbors via an oxygen atom. This means that silicon dioxide exists as a giant covalent structure in which large number of strong silicon-oxygen bonds have to be broken hence it is a solid . The strong bonds in three dimensions make it a hard, high melting point solid

CO_2 & SiO_2 are weakly acidic and covalent in nature

Reaction With water

Silicon dioxide doesn't react with water, because of the difficulty of breaking up the giant covalent structure.

Carbon dioxide does react with water to a slight extent to produce hydrogen ions.

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H^+_{(aq)} + HCO_3^{2-}{}_{(aq)}$$

The solution of carbon dioxide in water is sometimes known as carbonic acid.

Reaction With bases

Carbon dioxide reacts with sodium hydroxide solution in the cold to give either sodium carbonate or sodium hydrogen carbonate solution - depending on the reacting proportions.

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$

$$Na_2CO_{3(aq)} + H_2O_{(l)} + CO_{2(g)} \longrightarrow 2NaHCO_{3(s)}$$

White solid

Silicon dioxide is acidic and reacts with sodium hydroxide solution, but only if it is hot and concentrated. Sodium silicate solution is formed.

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_3\,(aq) + H_2O_{(l)}$$

. GeO_2, SnO_2, and PbO_2 are amphoteric in nature.

The basic nature of the dioxides

The dioxides react with concentrated hydrochloric acid first to give compounds of the type XCl_4 e.g

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

These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-}.

$$PbCl_{4(aq)} + 2Cl^-{}_{(aq)} \longrightarrow PbCl_6^{2-}{}_{(aq)}$$

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

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

The acidic nature of the dioxides

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

$GeO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Ge(OH)_6^{2-}{}_{(aq)}$

$SnO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Sn(OH)_6^{2-}{}_{(aq)}$

$PbO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Pb(OH)_6^{2-}{}_{(aq)}$

OR

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

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

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

The halides of group (IV) elements

+2 halides

Carbon and Silicon do not form +2 halides. Those of Germanium, Tin and lead can be prepared by heating the tetrachlorides with the free metal.

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

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

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

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

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

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

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

Note:

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

Explanation

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 soluble complex, tetrachloroplumbate (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.

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

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

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

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

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

To prepare lead(iv) chloride, use ice cold concentrated hydrochloric acid on lead(iv) oxide.

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

Note

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

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

Hydrolysis of the tetrachlorides

Carbon tetrachloride (CCl_4) does not undergo hydrolysis in water. This is due to the absence of a d sub shell in carbon and as such it cannot expand its octet.

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

$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$

$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$

White solid.

$GeCl_{4(l)} + 2H_2O_{(l)} \rightarrow GeO_{2(s)} + 4HCl_{(g)}$

$SnCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SnO_{2(s)} + 4HCl_{(g)}$

$PbCl_{4(l)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4HCl_{(g)}$

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 dichlorides.

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

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

Hydrides of group IV

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 and thus the Van der Waals forces of attraction holding the molecules together become progressively stronger as the 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 IIV elements

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

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

$SiH_{4(l)} + 4\,H_2O_{(l)} \rightarrow Si(OH)_{4(s)} + 4H_{2(g)}$

$GeH_{4(l)} + 4\,H_2O_{(l)} \rightarrow Ge(OH)_{4(s)} + 4H_2(g)$

$SnH_{4(l)} + 4\,H_2O_{(l)} \rightarrow Sn(OH)_{4(s)} + 4H_{2(g)}$

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

a) Its covalence is limited to 4 but others can have a maximum of 6. This is due to absence of vacant d-orbitals in carbon but others have.
b) 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.*
c) Its tetrachloride does not hydrolyze in water but tetra chlorides of other elements hydrolyze due to absence of vacant d-orbitals.
d) Carbon is the only element in group IV which forms only gaseous oxides.

Why carbon differs from other elements in group IV

a) It has the smallest radius in the group
b) Its electronegativity is the highest in the group
c) Carbon lacks a d-sub shell unlike other group members
d) Carbon is unable to show the inert pair effect and always exhibit a valency of 4 in almost all its compounds

Test for Lead (II) ions in solution

1) Use of sodium hydroxide solution
   Procedure
   To the solution containing the unknown cation is added sodium hydroxide solution dropwise until in excess.
   Observation

A white precipitate of Lead (II) hydroxide is formed. The precipitate dissolves in excess sodium hydroxide solution to form a cololourless due to the formation of plumbate (II) ions.

Equation

$Pb^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \longrightarrow Pb(OH)_{2(S)}.$

$Pb(OH)_{2(S)} + 2OH^{-}{}_{(aq)} \longrightarrow Pb(OH)_4{}^{2-}{}_{(aq)}$

2) Use of aqueous ammonia solution.

Procedure

To the solution containing the unknown cation is added aqueous ammonia dropwise until in excess.

Observation

In the presence of Lead (II) ions, a white precipitate of Lead (II) hydroxide is formed. The precipitate is insoluble in excess aqueous ammonia.

Equation

$Pb^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \longrightarrow Pb(OH)_{2(S)}.$

3) Use of dilute hydrochloric acid.

Procedure

To the solution containing the unknown cation is added a few drops of dilute hydrochloric acid.

Observation

A white needle like precipitate of lead (II) chloride is formed. The precipitate dissolves on heating but reappears on cooling.

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

4) Use of potassium chromate solution

Procedure

To the solution containing the unknown cation is added potassium chromate solution.

Observation

A yellow precipitate of lead (II) chromate is formed in the presence of Lead (II) ions.

Equation

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

5) Use of Potassium Iodide solution.

Procedure

To the solution containing the unknown cation is added a few drops of potassium iodide solution.

Observation

A yellow precipitate of lead (II) iodide is formed in the presence of lead (II) ions.

Equation

$Pb^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow PbI_{2(s)}.$

6) Use of dilute sulphuric acid.

Procedure

To the solution suspected to contain lead (II) ions is added dilute sulphuric acid.

Observation

A white precipitate of lead (II) sulphate is formed.

Equation

$Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)}$

7) Use of sodium carbonate solution

In the presence of Pb^{2+} ions a white precipitate of lead (II) carbonate is formed on addition of sodium carbonate solution.

$Pb^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow PbCO_{3(s)}$

Question

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, there is no precipitate. Explain this observation and write an ionic equation for the reaction in each case.

CHAPTER 6

GROUP (VII) ELEMENTS (HALOGENS)

Table 3: Physical properties of group VII elements

Element	*Atomic no*	*Outer elect conf*	*Melting pt/^{0}c*	*Boiling pt/0c*	*Bond energy /kcalmol-1*
Fluorine	*9*	*-$2s^2 2p^3$*	*-220*	*-188*	*37*
Chlorine	*17*	*-$3s^2 3p^3$*	*-101*	*-34*	*57.2*
Bromine	*35*	*-$4s^2 4p^3$*	*-7*	*58*	*45.4*
Iodine	*53*	*-$5s^2 5p^3$*	*114*	*183*	*35.6*

Physical properties of the halogens.

The halogens exist as diatomic molecules i.e. F_2, Cl_2, Br_2 and I_2.

Fluorine is a colourless gas, chlorine is a yellowish green gas, bromine is a reddish brown gas while iodine is a black (dark purple) solid at room temperature.

Halogens are highly reactive non-metals. They exist as diatomic molecules X_2 containing a covalent bond.

Due to their reactivity the elements do not occur in the free state but are always combined either among themselves or with other elements.

All the elements have 7 electrons in their outer most shells with general outer most electronic configuration of ns^2np^5 ($n= 2, 3, 4, 5$)

They can complete their octet by either gaining an electron to form an ionic bond or sharing electrons with other elements or themselves in a covalent bond.

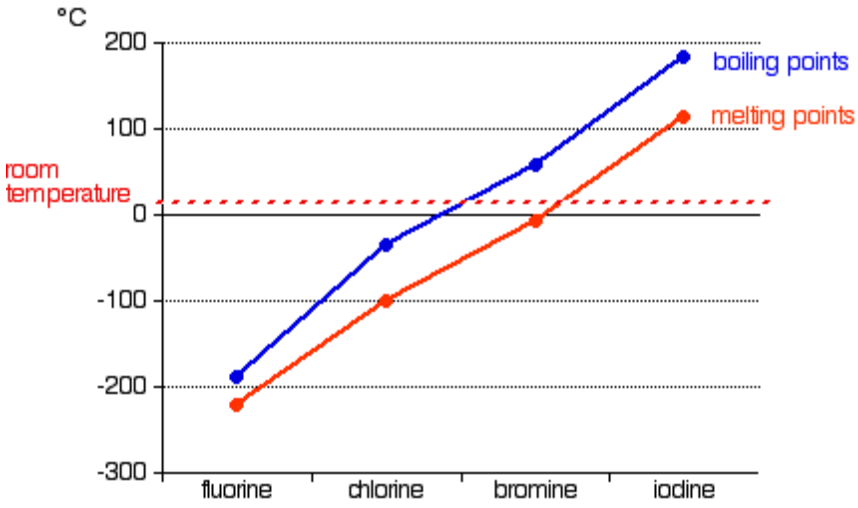
The melting and boiling points of the halogens are low but increase down the group.

<u>Explanation</u>

The diatomic molecules of halogens are held by weak intermolecular van der Waals forces of attraction. These forces become stronger with increasing molecular weight/ masses down the group.

In bromine and iodine, the forces are strong enough to bind their molecules to exist as liquid and solid respectively at room temperature. However, in fluorine and chlorine, the forces are not strong enough and as a result they exist as gases at room temperature.

Table 4: Melting and boiling points of group VII elemts

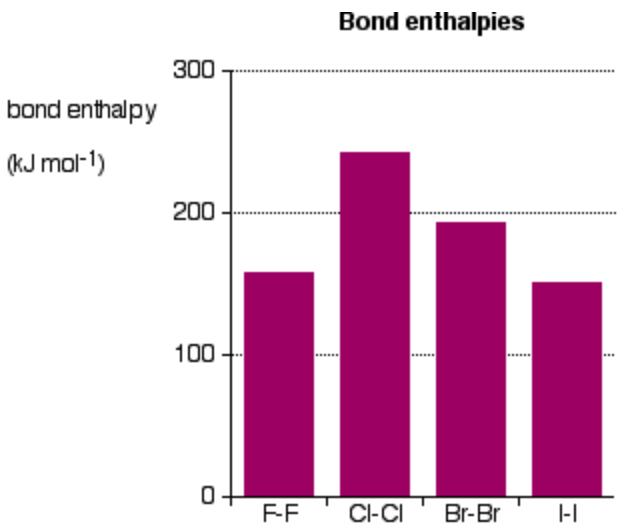


Bond dissociation energy

Bond energy is the energy required to break one mole of a covalent bond into its constituent gaseous atoms.

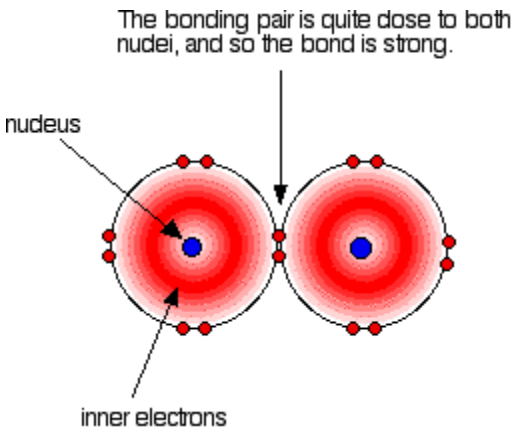
Or it's the energy released when one mole of a covalent bond is formed from its constituent gaseous atoms.

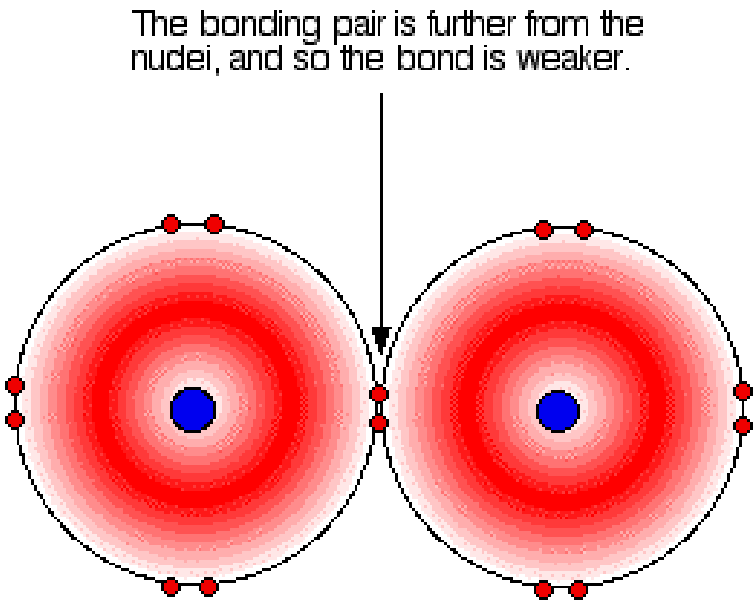
Bond dissociation energy of the diatomic molecules decreases down the group from chlorine to iodine. However, Fluorine has abnormally low bond dissociation energy.



This is due to small atomic radius of fluorine atom; the non bonding p- electrons present in Fluorine molecule are closer to one another as such repel each other strongly thus weakening the F-F bond.

The decrease in bond dissociation energy from Chlorine to Iodine is attributed to increase in atomic radius as the group is descended; the bonding electrons in the halogen-halogen bond are far from the nuclei of the halogens & are attracted less strongly due to the screening effect of the inner shells of electrons thus weakening the bond progressively





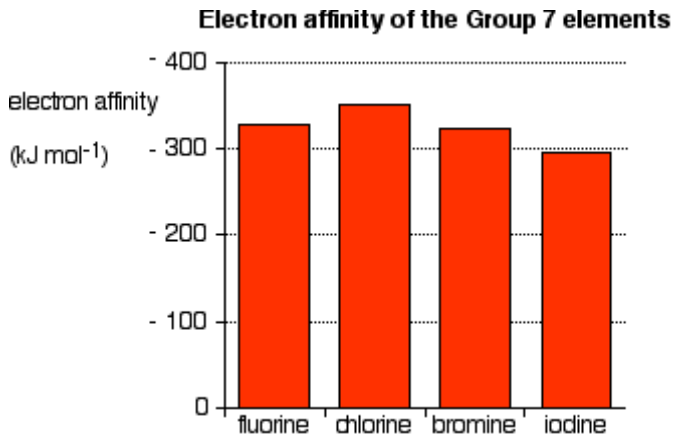
NB: The high reactivity of fluorine may be attributed to its low bond dissociation energy.

<u>Electron affinity of halogens</u>

E.A is the energy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of negatively charged gaseous ions.

$$X_{(g)} + e \longrightarrow X_{(g)}^{-}$$

The electron affinity is a more useful concept for the halogens than first ionisation energy because the halogens need only one electron to complete their octet to attain a noble gas like structure.



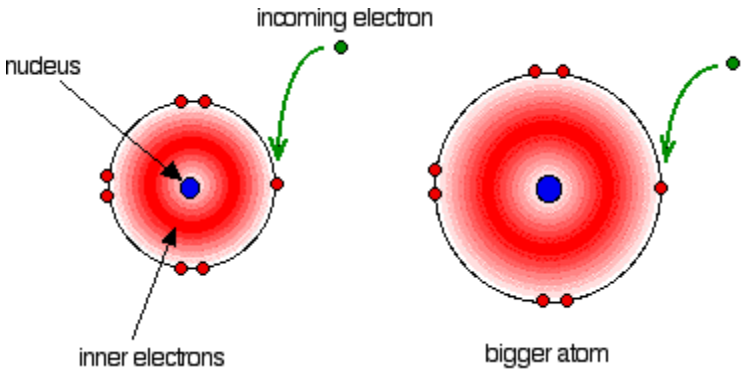
The electron affinity decreases numerically from Chlorine to Iodine. As the atomic radius increases down the group, the electron being added experiences a low attraction from the nucleus leading to a decrease in electron affinity.

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

<u>Explanation</u>

This is due to small atomic radius of fluorine atom; the 7 electrons in the outer most shell are too close to one another therefore the electron being added experiences greater repulsive forces from the electrons already present.

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.



Oxidizing properties of the halogens

Halogens are very good oxidizing agents with fluorine being the most oxidizing.

This is because fluorine is the most electronegative and has the highest positive value for its standard electrode potential.

It oxidises water to oxygen.

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4HF_{(aq)}$$

The standard electrode potential (E^{θ}) becomes less positive as the group is descended and so oxidising power decreases down the group.

Fluorine > Chlorine > Bromine > Iodine.

Oxidation states of the halogens

They all exhibit oxidation state of -1 by gaining an extra electron to complete their octet Fluorine is always o univalent due to absence of d-orbitals.

Other elements can show higher oxidation states due to availability of vacant d-orbitals which allow them to expand their octet.

Differences in the chemistry of Fluorine from other members of its group are:

Fluorine is has a fixed oxidation state of -1 while the other halogens have more than one oxidation states. This is because fluorine lacks a d sub shell while the other halogens have.

Hydrogen fluoride is a liquid while other hydrogen halides are gases at room temperature. This is due to the strong hydrogen bonds between hydrogen fluoride molecules as a result of high electronegativity of fluorine atom.

Fluorine forms the least acidic hydride whereas the hydrides of other members are fairly more acidic in aqueous solution.

This is due to the high strength of the H-F bond.

Fluorine is the most reactive halogen due to its low bond dissociation energy and high electronegativity.

Fluorine forms compounds with more ionic character due to its high electronegativity.

Fluorine forms hydride with the highest boiling point due to extensive hydrogen bonds.

Why does Fluorine show a difference?

Fluorine is the most electronegative halogen.

The bond dissociation energy of fluorine molecule is lower than expected.

Fluorine has a high positive value of standard electrode potential.

Fluoride ion having the smallest radius compared to other halides has the highest charge density and enthalpy of hydration.

Fluorine lacks a d sub shell.

General methods for preparing the halogens (excluding fluorine) in the laboratory

a) By the reaction between manganese (IV) oxide and concentrated halogen acid e.g.

$$4HCl_{(aq)} + MnO_{2(s)} \longrightarrow MnCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$$

$$4HBr_{(aq)} + MnO_{2(s)} \longrightarrow MnBr_{2(aq)} + 2H_2O_{(l)} + Br_{2(g)}$$

$$4HI_{(aq)} + MnO_{2(s)} \longrightarrow MnI_{2(aq)} + 2H_2O_{(l)} + I_{2(g)}$$

b) By the reaction between potassium manganate (VII) solution and hot concentrated halogen acid.
e.g.

$$2KMnO_{4(s)} + 16HCl_{(aq)} \longrightarrow 2KCl_{(aq)} + 2MnCl_{2(aq)} + 8H_2O_{(l)} + 5Cl_{2(g)}.$$

$$2KMnO_{4(s)} + 16HBr_{(aq)} \longrightarrow 2KBr_{(aq)} + 2MnBr_{2(aq)} + 8H_2O_{(l)} + 5Br_{2(g)}.$$

Reactions of halogens

In all their reactions the halogens act as oxidising agents. Hence, their reactivity decreases down the group.

1) <u>Reaction with water</u>
   a. Fluorine oxidises H_2O to O_2 gas in a very exothermic reaction.
   $$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4HF_{(aq)}$$

b. Chlorine dissolves in H_2O to form 'chlorine water' which is a mixture of two acids. No oxygen gas is evolved.

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HOCl_{(aq)}$$

c. Bromine is only slightly soluble in water.

$$Br_{2(l)} + H_2O_{(l)} \longrightarrow HBr_{(aq)} + HOBr_{(aq)}$$

d. Iodine is virtually insoluble in water. It is however soluble in potassium iodide solution due to the formation of a soluble complex the tri-iodide anion.

$$I_{2(s)} + I^-_{(aq)} \longrightarrow I_3^-{}_{(aq)}$$

Iodine is sparingly soluble in water because the energy involved in disrupting the weak van der walls forces in molecular iodine crystal lattice and the hydrogen bonds in water exceeds the energy changes involving the weak attraction between iodine and water molecules.

Note: **All halogens are more soluble in non-polar solvents such as CCl_4. Cl_2 gives a colourless solution. Br_2 a red solution and I_2 a violet one**

2) <u>Reaction with alkalis (sodium hydroxide or potassium hydroxide solution)</u>

This reaction depends on the conditions:

a) With cold and dilute alkalis the reactions are as below:

$$2KOH_{(aq)} + F_{2(g)} \longrightarrow 2KF_{(aq)} + F_2O_{(g)} + H_2O_{(l)}$$

$$2NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

$$2NaOH_{(aq)} + Br_{2(l)} \longrightarrow NaBr_{(aq)} + NaOBr_{(aq)} + H_2O_{(l)}$$

$$2KOH_{(aq)} + I_{2(s)} \longrightarrow KI_{(aq)} + KOIO_{(aq)} + H_2O_{(l)}$$

In hot solution the ClO^- ions undergo disproportionation reaction. Disproportionation reaction being a reaction in which is a species under go self oxidation & reduction reactions.

e.g.

$$3ClO^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + ClO_3^-{}_{(aq)}$$

$$6OH^-_{(aq)} + 3I_{2(s)} \longrightarrow 5I^-_{(aq)} + IO_3^- + 3H_2O_{(l)}$$

Iodine is reduced to iodide ions as its oxidation state decreases from zero to -1 and at the same time its oxidised to iodate ions as its oxidation state increases from 0 to +5.

b) With hot and concentrated alkali, reactivity decreases down the group.

$$4NaOH_{(aq)} + 2F_{2(g)} \longrightarrow 4NaF_{(aq)} + O_{2(g)} + 2H_2O_{(l)}$$

$$6KOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5KCl_{(aq)} + KClO_{3(aq)} + 3H_2O_{(l)}$$

Note

Other halogens react in a similar manner.

Compounds of the halogens

Hydrides of group VII elements

a) Boiling points of hydrides increase from Hydrogen chloride through Hydrogen bromide to Hydrogen bromide but that of Hydrogen fluoride is abnormally high.

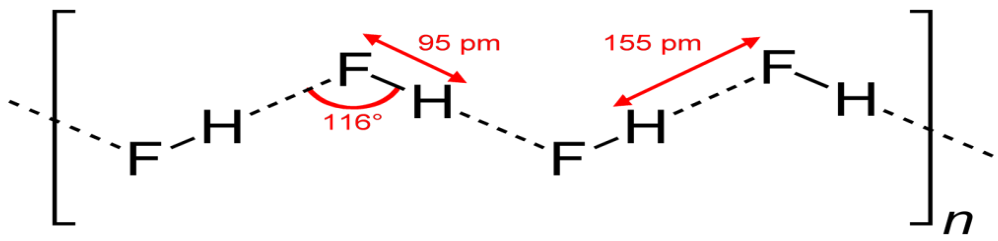
Hydrogen halide	*Boiling point/ ^0C*
HF	*19*
HCl	*-85*
HBr	*-66*
HI	*-36*

The increase in boiling point from Hydrogen chloride to Hydrogen iodide is attributed to increasing molecular mass of the halogens.

This in turn increases the strength of van der Waals forces of attraction between their molecules hence increasing the boiling point of Hydrogen chloride to Hydrogen iodide.

Hydrogen fluoride however, has abnormally high boiling point because Fluorine atom has a very small atomic radius and high electronegativity, as a result it forms a more polar

Hydrogen fluoride bond and its molecules associate through strong intermolecular hydrogen bonds which require greater amount of energy to break.



<u>The acidity of the hydrides</u>

The acidity of the hydrides is in the order *H-F <H-Cl< H-Br< H-I.*

H-F is the weakest acid because the H-F bond is very strong as a result of small atomic radius and high electronegativity of Fluorine atom.

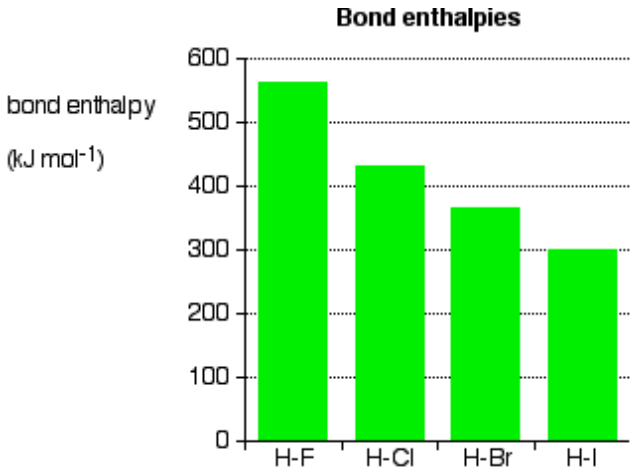
It is weakly dissociated in solution releasing fewer H^+ ions.

In addition, the presence of hydrogen bonding between HF molecules and water molecules inhibits the ionization of HF in aqueous solution.

However, as the group is descended, electronegativity decreases whereas atomic radius increases. As such the H- halide bonds become progressively longer and weaker. They dissociate in solution releasing more hydrogen ions.

Bond energy/enthalpy of the hydrides generally decreases in moving from Hydrogen fluoride to Hydrogen iodide i.e.

H-F > H-Cl > H-Br > H-I



As the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker.

Fluorine is the most electronegative atom with the smallest atomic radius thus the H-F bond is the most polar. Iodine is the least electronegative with the largest atomic radius as a result the H-I bond is the least polar. The greater the extent of polarity, the greater the ionic character in the bond and therefore the stronger the bond.

Reactions of the halogen acids

All the halogens acids undergo reactions typical of all acids

e.g.

They react with carbonates and hydrogen carbonates giving off carbon dioxide gas

They react with metals producing corresponding salts and hydrogen gas

They neutralise bases forming salts and water

Note

For hydrofluoric acid, as well as undergoing reactions typical of all acids, it reacts with silicon dioxide and silicon forming fluorosilic acid

$$6HF_{(aq)} + SiO_{2(s)} \longrightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)}$$

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

Reaction of halogen acids with concentrated sulphuric acid

Hydrofluoric acid and hydrochloric acid not react with concentrated sulphuric acid

Hydrobromic acid and hydroiodic acid react with hot concentrated sulphuric acid

$$HBr(aq) + H_2SO_4(aq) \longrightarrow Br_2(g) + SO_2(g) + 2H_2O_{(l)}$$

$$Hl(aq) + H_2SO_4(aq) \longrightarrow l_2(g) + SO_2(g) + 2H_2O_{(l)}$$

Oxy acids of chlorine

Table 5: Oxy acids of chlorine

Formula	structure	Name
HOCl	*H-O-Cl*	*Hypochlorous acid (chlorous (I) acid)*
$HClO_2$	*HOCl=O*	*Chlorous acid (chlorous (III) acid)*
$HClO_3$	$HOClO_2$	*Chloric acid (chlorous (V) acid)*
$HClO_4$	$HOClO_3$	*Perchloric acid (chlorous (VII) acid*

Note

Salts of hypochlorous acid *(HOCl)* are called hypochlorites e.g.

a) Sodium hypochlorite *(NaOCl)* present in liquid bleaches e.g. JIK
b) Calcium hypochlorite $(Ca(OCl)_2)$ present in bleaching powder

The percentage of available chlorine in either JIK or bleaching powder can be determined in the laboratory.

Procedure

The JIK or bleaching powder is added to ethanoic acid or hydrochloric acid. Chlorine gas is liberated and its passed through a solution of potassium iodide solution and iodine is liberated.

The liberated iodine is then titrated against a standard solution of sodium thiosulphate using starch as indicator.

The volume of the thiosulphate solution used is noted.

Equation of reactions taking place

JIK (NaOCl and NaCl)

$NaOCl_{(aq)} \longrightarrow Na^{+}_{(aq)} + ClO^{-}_{(aq)}$

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

On addition of an acid to JIK the reaction below takes place,

$OCl^{-}_{(aq)} + Cl^{-}_{(aq)} + H^{+}_{(aq)} \longrightarrow H_2O_{(l)} + Cl_{2(g)}$

Available chlorine

Then,

$Cl_{2(g)} + 2I^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + I_{2(aq)}$

$Cl_{2(g)} + 2I^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + I_{2(aq)}$

$S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^{-}(aq)$

<u>Acid strength of the oxyacids</u>

<u>Trend</u>

The acidity of the oxyacids in aqueous solution increase with increase in the number of oxygen atoms present i.e. hypochlorous acid (HOCl) is the least acidic oxyacid and chloric (vii) acid ($HClO_4$) the most acidic in aqueous solution.

<u>Explanation</u>

Order of acidity is $HOCl < HOClO < HOClO_2 < HOClO_3$

As the number of the oxygen atoms increase, the H-O bond becomes weaker and in aqueous solution the bond easily ionise producing more H+ ions in solution.

Test for Chlorides, Bromides and Iodides ions

1) <u>Use of silver nitrate solution</u>

   <u>Procedure</u>

   To the solution containing the unknown anion is added silver nitrate solution.

   <u>Observation</u>

a) In the of chloride ions a white silver chloride is formed. The precipitate dissolves in excess aqueous ammonia due to the formation of a soluble complex called diammine silver (I) ions.

Equation

$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$ *white precipitate.*

$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)_2^{+}{}_{(aq)} + Cl^{-}_{(aq)}$

Soluble complex.

b) In the presence of bromide ions a pale yellow precipitate of silver bromide is formed. The precipitate dissolves in excess aqueous ammonia due to the formation of a soluble complex.

Equation

$Ag^{+}_{(aq)} + Br^{-}_{(aq)} \longrightarrow AgBr_{(s)}$ *pale yellow precipitate.*

$AgBr_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)_2^{+}{}_{(aq)} + Br^{-}_{(aq)}$

Soluble complex.

c) In the presence of iodide ions, a yellow precipitate of silver iodide is formed. The precipitate is insoluble in excess aqueous ammonia.

Equation

$Ag^{+}_{(aq)} + I^{-}_{(aq)} \longrightarrow AgI_{(s)}$ *yellow precipitate.*

2) Use of lead (II) nitrate or lead (II) ethanoate solution.

Procedure

To the solution containing the unknown anion is added lead (II) nitrate or lead (II) ethanoate solution.

Observation

a) In the presence of chloride ions a white precipitate of lead (II) is formed. The precipitate dissolves on cooling but reappears on cooling.

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

b) In the presence of bromide ions a white precipitate of lead (II) is formed. The precipitate dissolves on warming but reappears on cooling

$Pb^{2+}_{(aq)} + 2Br^{-}_{(aq)} \longrightarrow PbBr_{2(s)}$

c) In the presence of iodide ions a pale yellow precipitate of lead (II) iodide is formed. The precipitate dissolves on warming but reappears on cooling

$$Pb^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow PbI_{2(s)}$$

3) Use of chlorine water and tetrachloromethane

Procedure

To the solution containing the unknown anion is added Chlorine water followed by 2-3 drops of tetrachloromethane

Observation

a) In the presence of chloride ions, there is no observable change.

b) In the presence of bromide ions, a brown colour appears in the organic liquid.

c) In the presence of iodide ions, a purple/violet colour appears in the organic liquid.

4) Use of concentrated sulphuric acid

Procedure

To the a few grams of the solid containing the unknown anion is added concentrated sulphuric acid

Observation

a) In the presence of chloride ions, hydrogen chloride gas is evolved (white fumes).
b) In the presence of bromide ions, bromine gas (brown) and hydrogen bromide gas is evolved.
c) In the presence of iodide ions, iodine vapour (purple) and hydrogen iodide gas is evolved.

5) Use of copper (II) sulphate solution

Procedure

When the reagent is added to a solution containing iodide ions, a white precipitate of copper (I) iodide and a brown solution of iodine is formed.

Equation

$$Cu^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$$

CHAPTER 7

PERIOD 3 ELEMENTS IN THE PERIODIC TABLE

Table 6: Physical properties of group III elements

Element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Atomic no	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*
Outer electronic conf	$-3s^1$	$-3s^2$	$-3s^2\ 3p^1$	$-3s^2 3p^2$	$-3s^2 3p^3$	$-3s^2 3p^4$	$-3s^2 3p^5$	$-3s^2\ 3p^6$
Melting point/^{0}C	*97.8*	*650*	*660*	*1410*	*44*	*119*	*-101*	*-189*
Atomic radius/^{0}A	*1.57*	*1.36*	*1.26*	*1.17*	*1.10*	*1.04*	*0.99*	
1st I.E/kjmol-1	*496*	*737*	*577*	*786*	*1012*	*999*	*1255*	*1521*
1st E.A/kjmol-1	*-20*	*67*	*-30*	*-135*	*-60*	*-200*	*-364*	

Revision question

State and explain the trend in the variation of the following across the 3rd period in the periodic table

a) Atomic radius
b) 1st ionization energy
c) 1st electron affinity
d) Electronegativity
e) Electropositivity
f) Melting point

Compounds of period 3 elements

1) Chlorides

Element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
Formula of chloride	*NaCl*	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3,PCl_5	S_2Cl_2	Cl_2
Type of bonding in the chloride	*Ionic*	*Ionic*	*Covalent*	*Covalent*	*Covalent*	*Covalent*	*Covalent*

Sodium chloride and magnesium chloride are ionic chlorides with giant structures. They have high melting points.

The melting point of sodium chloride is higher than for magnesium chloride which in turn is higher than for aluminium chloride.

Explanation

Ionic compounds tend to have higher melting points than covalent compounds.

From *NaCl*, through $MgCl_2$ to $AlCl_3$, the cationic radius decreases from Na^+, through Mg^{2+} to Al^{3+} as the charge increases from +1 to +3.

This leads to an increase in cationic charge density from Na^+ to Al^{3+}.

Aluminium ion with the highest charge density greatly polarizes the electron clouds of the chloride ions to which it is bonded making aluminium chloride predominantly covalent.

Magnesium ion also polarizes the electron clouds of the chloride ions to which it is bonded but the extent of polarization is less than in aluminium chloride. Magnesium chloride is therefore predominantly ionic.

Sodium ion with the least polarizing power makes sodium chloride the most ionic chloride in the period and with the highest melting point, followed by magnesium chloride and then aluminium chloride.

Note

The other chlorides in the period; namely $SiCl_4$, PCl_3, PCl_5, S_2Cl_2 and Cl_2 are covalent molecules with weak intermolecular van der waals forces of attraction in them. The magnitude of these forces increasing with increase in molecular mass. They all therefore have low melting and boiling points.

Reactions of the chlorides with water

a) Sodium chloride dissociates in water to give a neutral solution i.e the P^H of the resultant solution is 7.

$$NaCl_{(aq)} + aq \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

b) Magnesium chloride hydrolyses in water to form an acidic solution

$$MgCl_{2(s)} + H_2O_{(l)} \rightleftharpoons Mg(OH)Cl_{(s)} + HCl_{(aq)}$$

c) Aluminium chloride in water hydrolyses to form a solution whose P^H is less than 7

$$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow Al(H_2O)_6^{3+}{}_{(aq)} + 3Cl^-{}_{(aq)}$$

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

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

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

Over all equation:

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

White ppt

Silicon (IV) chloride reacts with water producing silicondioxide and hydrochloric acid. The P^H of the resultant solution is therefore less than 7.

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

White solid

a) The rest of the chlorides react with water to form acidic solutions.

$$PCl_{3(l)} + H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

$$PCl_{5(l)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

$$S_2Cl_{2(l)} + 2H_2O_{(l)} \longrightarrow 3S_{(s)} + 4HCl_{(aq)} + SO2_{(g)}$$

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HOCl_{(aq)}$$

2) <u>The oxides of period 3 elements</u>.

Eement	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
Oxide	Na_2O, Na_2O_2	MgO	Al_2O_3	SiO_2	P_2O_3, P_2O_5	SO_2, SO_3	Cl_2O Cl_2O_7

Type of bonding	*ionic*	*ionic*	*Ionic*	*covalent*	*covalent*	*Covalent*	*covalent*

The oxide of sodium, magnesium and aluminium are ionic compounds and conduct electricity in molten state due the presence of free ions. They have giant ionic structures with high melting points.

Silicon dioxide has a giant molecular structure and therefore has a very high melting point.

The rest of the oxides have simple molecular structures with weak intermolecular van der waals forces and hence have low melting and boiling points.

<u>Reactions of the oxides with water</u>

a) The oxides of sodium and magnesium react with water forming alkaline solutions. Aluminium oxide is however insoluble in water.

$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$

$Na_2O_{2(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_2O_{2\,(aq)}$

$MgO_{(s)} + H_2O_{(l)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$

b) Silicon dioxide does not react with water. Being acidic, it however reacts with alkalis forming silicates

$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_3\,(aq) + H_2O_{(l)}$

c) The rest of the oxides react with water to form acidic solutions

$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$

$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$

$P_2O_{3(g)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)}$

$P_2O_{5(g)} + 3H_2O_{(l)} \longrightarrow H_3PO_{4(aq)}$

$Cl_2O_{(g)} + H_2O_{(l)} \longrightarrow 2HOCl_{(aq)}$

$Cl_2O_{7(g)} + H_2O_{(l)} \longrightarrow 2HClO4_{(aq)}$

The Hydrides of period 3

Table 7: The Hydrides of period 3 elements

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

Hydrolysis of the hydrides in water

$NaH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g}$

$MgH_{2(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} + H_{2(g)}$

$AlH_{3(s)} + 3H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + 3H_{2(g)}$

$SiH_{4(g)} + 2H2O_{(l)} \longrightarrow SiO_{2(g)} + 4H_{2(g)}$

$H_2S_{(g)} + 2H_2O_{(l)} \longrightarrow S^{2-}{}_{(aq)} + 2H_3O^+{}_{(aq)}$

$HCl_{(g)} + H_2O_{(l)} \longrightarrow Cl^-{}_{aq)} + H3O^+{}_{(aq)}$

Note

PH_3 is not affected by water because it is non polar. This is because phosphorous and hydrogen have similar electronegativity values.

ALUMINIUM

The ore of aluminium

a) Bauxite; $Al_2O_3.2H_2O$

b) Cryolite; Na_3AlF_6

Extraction of aluminium

Aluminium is commonly extracted from its ore called bauxite.

Impurities found in bauxite are:

- *Silica*, SiO_2
- *iron(iii) oxide*, Fe_2O_3

The extraction process is divided into two stages.

1) Purification of the impure bauxite

This involves purifying the impure bauxite to form pure aluminium oxide.

The ore is first roasted at a low temperature to convert the iron (ii) oxide to iron (iii) oxide. The roasted product is then crushed to powder form and dissolved in concentrated sodium hydroxide solution.

The dissolution in concentrated sodium hydroxide is to separate iron (iii) oxide from the ore.

Being an amphoteric oxide, Al_2O_3 and the acidic oxide SiO_2 dissolve in the sodium hydroxide solution as shown by the equations below

$$Al_2O_{3(s)} + 2OH^-(aq) + 3H_2O(l) \longrightarrow 2\,Al(OH)_4^-(aq)$$

$$SiO_{2(s)} + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

The iron (iii) oxide being basic does not dissolve and is eliminated by filtering off.

Aluminium hydroxide is then obtained from the sodium aluminate solution by either:

i. Adding a little prepared aluminium hydroxide to aluminate solution to precipitate more aluminium oxide; a process referred to as seeding.

$$Al(OH)_4^-{}_{(aq)} \longrightarrow Al(OH)_{3(s)} + OH^-{}_{(aq)}$$

ii. bubbling CO_2 gas through the filtrate (aluminate solution)

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

The aluminium hydroxide from either method is filtered off, washed and dried. The dry aluminium hydroxide is then heated to form aluminium (III) oxide.

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

2) <u>Electrolysis of the pure aluminium oxide</u>

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

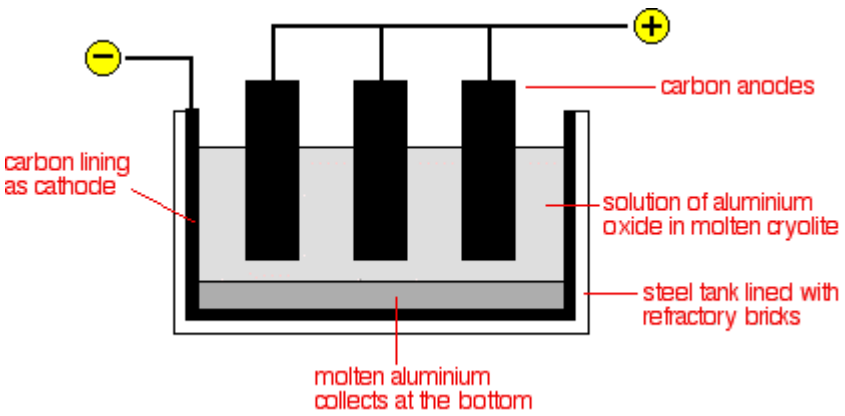
The molten aluminium oxide is then electrolyzed at a temperature between 800-900 ^{0}c at a high current density between graphite electrodes.

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

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

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

The electrolysis cell



<u>Note</u>

The oxygen gas produced at the anode oxidizes the graphite (carbon) anode and therefore it is replaced (renewed) from time to time.

<u>Reactions of aluminium</u>

a) Reaction with water.

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

$$2Al_{(s)} + 3H_2O_{(g)} \longrightarrow Al_2O_{3(s)} + 3H_{2(g)}$$

b) Reaction with chlorine.

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

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)}$$

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

c) Reaction with alkalis.

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

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

d) Reaction with acids.

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

$$2Al_{(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$$

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

$$2Al_{(s)} + 6H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3SO_{2(g)} + 6H_2O_{(l)}.$$

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 hexaaqua 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:

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

$$[Al(H_2O)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_4(OH)_2]^+_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_4(OH)_2]^+_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_3(OH)_3]_{(s)} + H_3O^+_{(aq)}$$

Over all equation:

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

The hydroxonium ions produced make the resultant solution acidic with P^H 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.

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2\,Al(OH)_4^-{}_{(aq)}$$

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow Al(OH)_4^-{}_{(aq)}$$

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

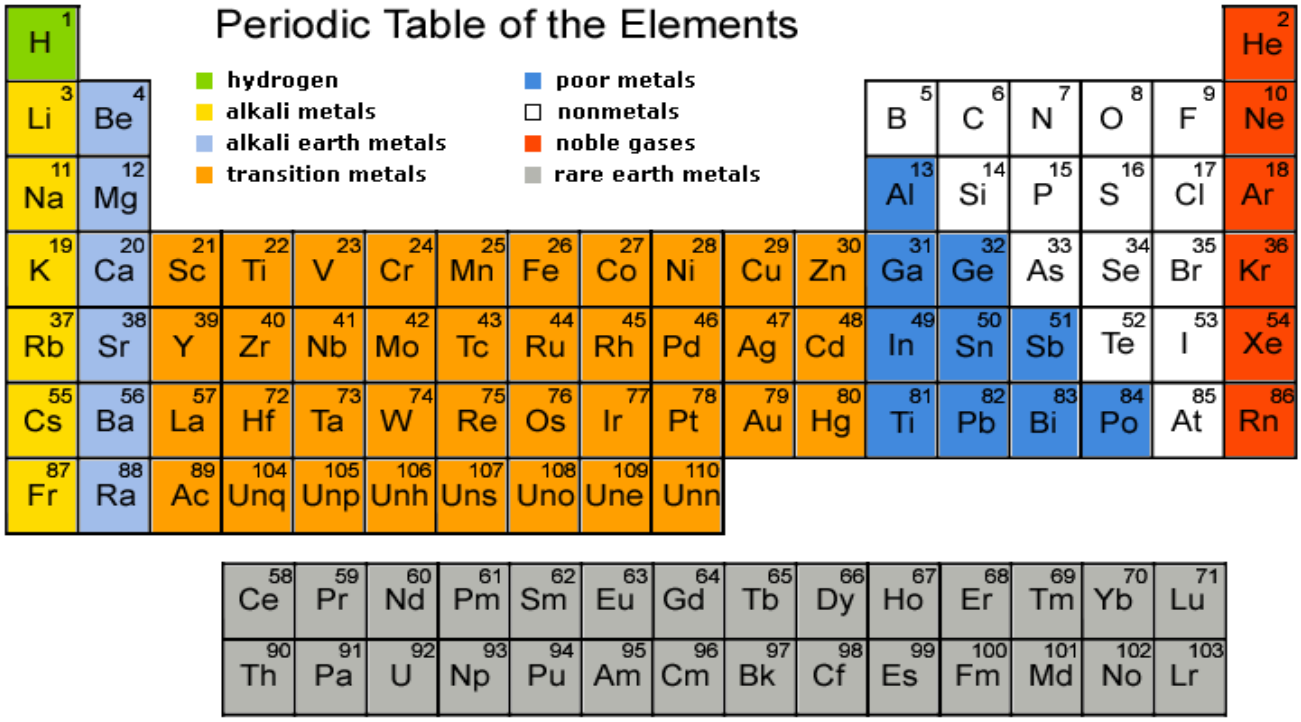
Some uses of aluminium include:

Aluminium is used for:	Useful properties
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

CHAPTER 8

TRANSITION ELEMENTS

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



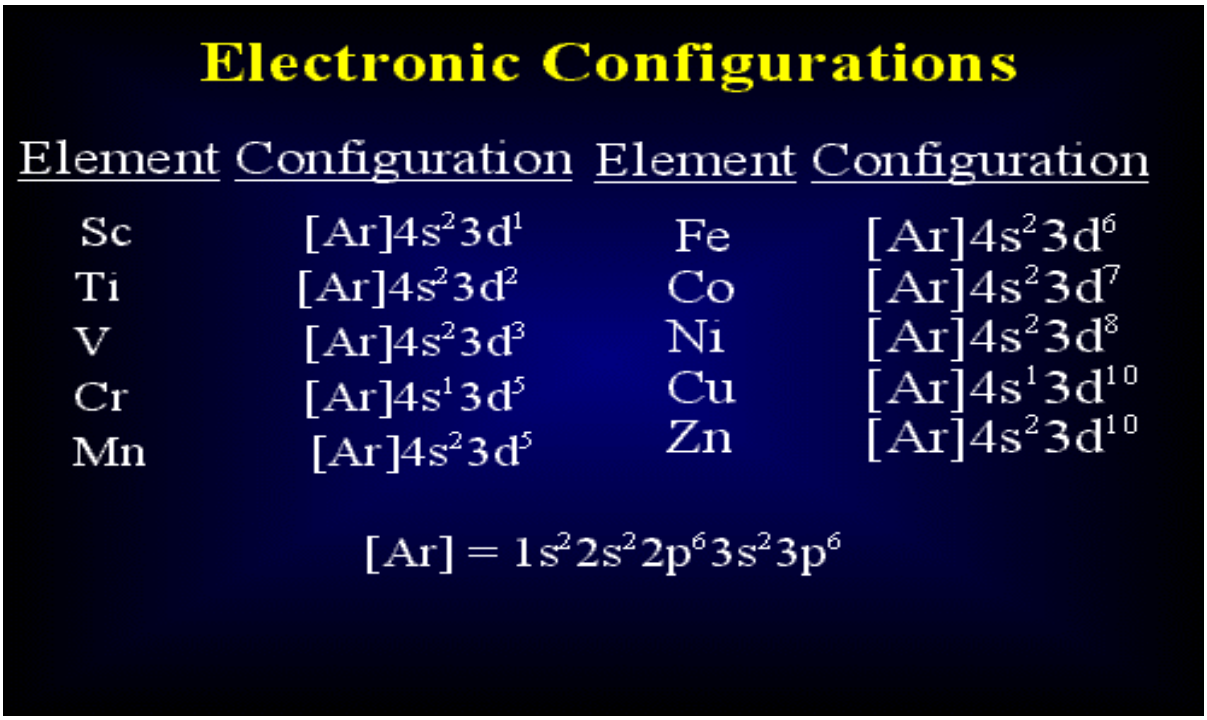
<u>d-block elements</u>:

A d-block element is one in which the inner 3d sub-shell is in the process of filling up with electrons after the outermost 4s sub-shell(which has a lower energy) has already been filled.

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 forms at least one ion with a partially filled 3d sub shell. All transition elements are d-block elements.



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 stable arrangement than $[Ar]\ 3d^4 4s^2$

This is because the former configuration has 3d sub shell half filled with electrons and therefore energetically more stable than the latter configuration where the 3d has only 4 electrons.

Unpaired electrons experience minimum repulsion between them.

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 energetically stable

Configuration of selected ions

Sc^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6$
Cr^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
Mn^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
Mn^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$
Fe^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
Fe^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
Cu^{+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
Cu^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
Zn^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

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.

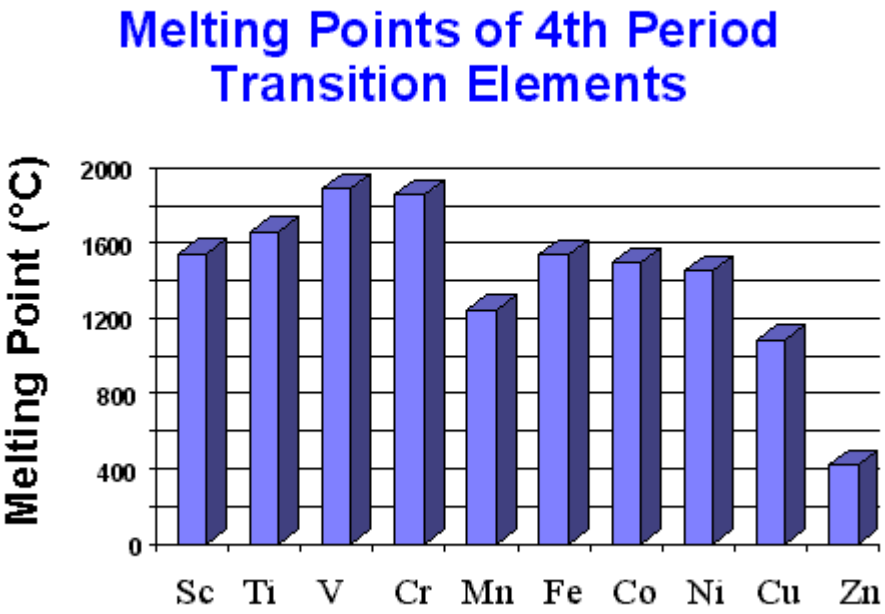
Thus when the 3d sub shell is occupied, the electrons in it repel the 4s-electrons further from the nucleus and in the process the energy of the 4s electrons increase more than for the 3d electrons. Therefore the 4s electrons are lost before the 3d electrons.

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 in metallic bond formation. The greater the number of electrons contributed to the metallic bond, the higher the melting point. Transition elements therefore have high melting and boiling points.



is is attributed to the stability of half-filled 3d-orbitals, electrons therefore being less available for metallic 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.

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

<u>Exercise</u>

The atomic numbers and melting points of some d-block elements are as follows**:**

Element	*Sc*	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*
Atomic.No	*21*	*22*	*23*	*24*	*25*	*26*	*27*	*28*	*29*
M.Point(^{0}C)	*1540*	*1680*	*1900*	*1890*	*1240*	*1540*	*1500*	*1450*	*1080*

i) Plot a graph of the melting points against atomic numbers. (3mks)

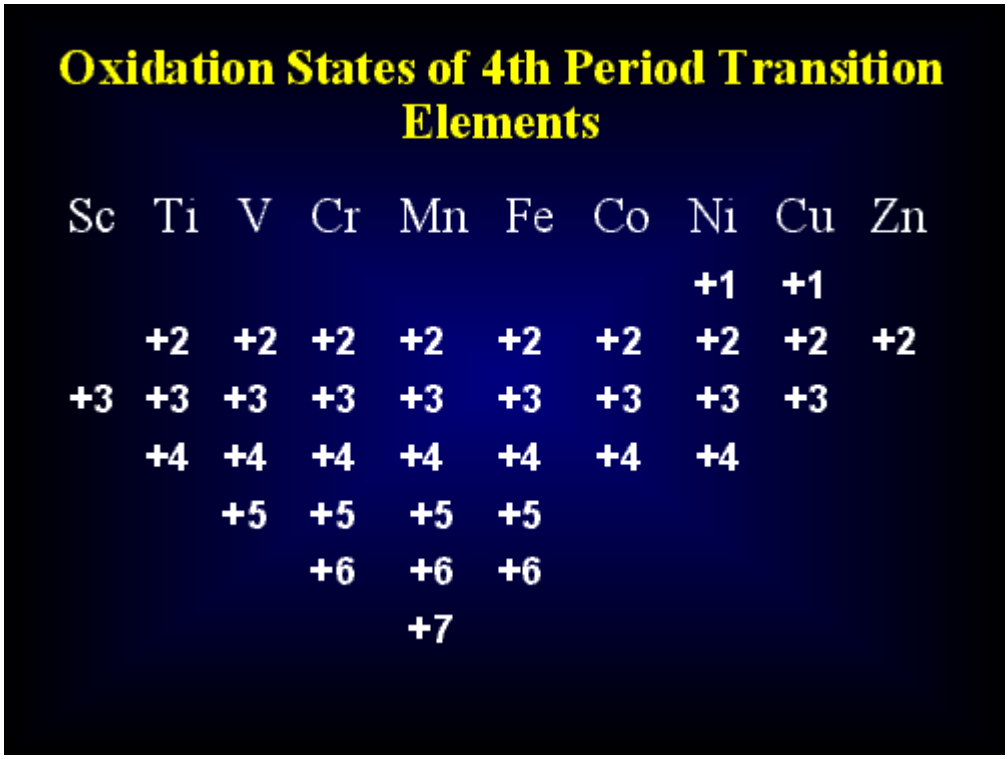
ii) Explain the shape of your graph.(4marks)

2) Variable oxidation states**.**

The variable oxidation states exhibited by transition elements are 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.



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EXERCISE

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 .

In reactions involving gases, 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 and in the process reducing the activation energy for the reaction.

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:

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

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

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

IV. 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 overall positive charge

Formula	*Colour*	*Name of complex ion*	*Coordination number*	*Ox. St. of metal ion*
$Cu(H_2O)_4^{2+}$	*Blue*	*Tetra-aqua copper(ii)ion*	*4*	*+2*
$[Cu(NH_3)_4]^{2+}$		*Tetra-ammine copper(ii)ion*	*4*	*+2*
$[Co(H_2O)_6]^{2+}$	*Pink*	*Hex-aqua cobalt(ii) ion*	*6*	*+2*
$[Ni(H_2O)_6]^{2+}$	*Green*	*Hex-aqua nickel(ii) ion*	*6*	*+2*
$[Cr(H_2O)_6]^{3+}$	*Violet*	*Hex-aqua chromium(iii)ion*	*6*	*+3*
$[Cr(NH_3)_6]^{3+}$	*Yellow*	*Hex-ammine chromium(iii)ion*	*6*	*+3*
$[Cr(NH_3)_4Cl_2]^{+}$		*Tetra-ammine dichlorochromium(iii)ion*	*6*	*+3*

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

Formula	*Color*	*Name of complex*	*Coordination number*	*Oxidation state of cation*
$[CuCl_4]^{2-}$	*Yellow*	*Tetra chlorocuprate(ii)ion*	*4*	*+2*
$[CoCl_4]^{2-}$	*Blue*	*Tetra chlorocobaltate(ii)ion*	*4*	*+2*
$[Zn(OH)_4]^{2-}$	*Colorless*	*Tetra hydroxozincate(ii)ion*	*4*	*+2*
$[Fe(CN)_6]^{3-}$		*Hexacyanoferrate(iii) ion*	*6*	*+3*
$[Fe(CN)_6]^{4-}$		*Hexacyanoferrate(ii) ion*	*6*	*+2*
$[Ni(CN)_4]^{2-}$		*Tetracyanonickelate(ii)ion*	*4*	*+2*

Neutral complexes are those that carry no charge.

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

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

<u>Exercise</u>

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 3d'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

QUESTION

a) Write the electronic configuration of the following species (atomic number Cr is 24):

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 Chromium (iii) ions, 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) $Cr^{6+}: 1S^2 2S^2 2P^6 3S^2 3P^6$

Note

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

Grey green precipitate, soluble in excess forming a green solution.

Equations

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

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

d)

With Air (oxygen)

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

$4Cr_{(s)} + 3O_{2(g)} \longrightarrow 2Cr_2O_{3(s)}$ green solid.

With water.

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

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

With acids.

Chromium reacts with dilute hydrochloric acid forming green chromium(iii) chloride solution and liberating hydrogen gas.

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

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.

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

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

Ionically:

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

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

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

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

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

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

Note:

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.

With chlorine

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

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

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

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

With sodium hydroxide solution

Chromium dissolves in sodium hydroxide solution giving:

- Effervescence of a colorless gas that burns with a pop sound.
- a green solution.

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

Compounds of Chromium

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

The most stable oxidation state of chromium is +3.

The acidity of the hexaqua ions

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

The resultant solution is acidic due to hydrolysis reaction

.i.e.

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

$$[Cr(H_2O)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_4(OH)_2]^+_{(aq)} + H_3O^+_{(aq)}$$

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

Over all equation:

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

Green ppt.

The hydroxonium ions produced make the resultant solution acidic with P^H less than 7 and a green solid is observed due to the formation of hydrated chromium (iii) hydroxide.

If sodium carbonate solution is added to an aqueous solution of chromium (iii) salts, bubbles of a colorless gas that turns lime water milky is observed due to the carbon dioxide gas produced by the reaction between the hydroxonium ions and the carbonate ions.

$$CO_3^{2-}{}_{(aq)} + 2H^+_{(aq)} \longrightarrow CO_{2\,(g)} + H_2O_{(l)}$$

If magnesium ribbon is added to an aqueous chromium (iii) salt, a colorless gas that burns with a pop sound is liberated due to the reaction between the acidic solution and magnesium metal.

$$Mg_{(s)} + 2H_3O^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2\,(g)} + 2H_2O_{(l)}$$

or

$$Mg_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2\,(g)}$$

<u>Note</u>

Like chromium (iii) salts in aqueous solution, aqueous solution of aluminium and iron (iii) salts also undergo hydrolysis reactions to produce acidic solutions.

<u>Chromium (iii) oxide, Cr_2O_3</u>

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

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

It is an amphoteric oxide.

It reacts with dilute mineral acids to form corresponding Cr^{3+} salt and with sodium hydroxide to forming the soluble complex $Cr(OH)_6^{3-}{}_{(aq)}$

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

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

Green solution

<u>Chromium (iii) hydroxide</u>

It's a green solid formed when little sodium hydroxide is added to a solution containing Cr^{3+} ions. It's an amphoteric hydroxide; reacting with dilute acids forming corresponding Cr^{3+} salts and with aqueous alkalis forming the complex $Cr(OH)_6^{3-}{}_{(aq)}$.

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

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

<u>Hydrated Chromium (iii) Chloride.$CrCl_3.6H_2O$</u>

This salt of chromium exhibits hydration isomerism i.e. existence of compounds with the same molecular formula but different structural formulae due to the difference in the number of water molecules directly bonded to the central chromium (iii) ion.

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

i. $[Cr(H_2O)_6]^{3+}\ 3Cl^-$
(Hexaquachromium (iii) chloride)

ii. $[Cr(H_2O)_5Cl]^{2+}.2Cl^-.H_2O$
(Chloropentaqua chromium (iii) chloride monohydrate)

iii. $[Cr(H_2O)_4Cl_2]^+.Cl^-.2H_2O$
(Dichlorotetraaqua chromium (iii) chloride dihydrate)

Identification/test for the isomers

1) Using silver nitrate solution:

- The first isomer precipitates 3moles of silver chloride because all the $3Cl^-$ ions can be precipitated because they are not directly bonded to the central metal cation,
- The 2nd isomer precipitates 2moles of silver chloride per mole of the isomer.
- The 3rd isomer precipitates 1mole of silver chloride per mole of the isomer.

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. e.g.

K_2CrO_4 and Na_2CrO_4.

A Chromate ion has a tetrahedral structure

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

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

Orange yellow

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

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

ALUMS

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

The 1st M is a group (I) metal e.g. Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+ etc

The 2nd M is a group (III) metal or a metal bearing a +3 charge e.g. Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+} etc

Examples of common alums are:

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

Its solution in water is acidic because the chromium (iii) ions undergo hydrolysis making the solution acidic.

The complex ion is acting as an acid by donating a hydrogen ion to water molecules in the solution.

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

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

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

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

Over all equation:

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

The accumulation of hydroxonium ions renders the resultant solution acidic.

If aqueous sodium carbonate is added, an efferverscence of a colorless gas which turns lime water milky is formed and a greeen solid.

$$2[Cr(H_2O)_6]^{3+} + 3CO_3^{2-} \longrightarrow 2[Cr(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$$

2) Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$

3) Ammonium alum $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

Preparation of Chrome Alum

By bubbling sulphur dioxide gas through an acidified potassium dichromate solution, chrome alum is formed.

$$SO_{2\,(g)} + H2O_{(l)} \longrightarrow H_2SO_{3\,(aq)}$$

$$H_2SO_{3\,(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$$

$$SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \quad 2e$$

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

The ions present after the above reactions are in the correct proportion for the formation of chrome alum on crystallizing.

Similarities between the chemistry of chromium and lead

$Cr^{3+}$and Pb^{2+} form complex with sodium hydroxide solution.

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

$$Cr(OH)_{3\,(s)} + 3\,OH^-{}_{(aq)} \longrightarrow [Cr(OH)_6]^{3-}{}_{(aq)}$$

$$Pb^{2+}{}_{(aq)} + 2\,OH^-{}_{(aq)} \longrightarrow Pb(OH)_{2\,(s)}$$

$$Pb(OH)_{2\,(s)} + 2\,OH^-{}_{(aq)} \longrightarrow [Pb(OH)_4]^{2-}{}_{(aq)}$$

Both their oxides in higher oxidation states are acidic.

$$CrO_{3(s)} + 2NaOH_{(aq)} \longrightarrow Na_2CrO_{4(aq)} + H_2O_{(l)}$$

$$PbO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2PbO_{3(aq)} + H_2O_{(l)}$$

Their oxides in higher oxidation states are strong oxidizing agents.

$$CrO_{3(s)} + Al_{(s)} \longrightarrow Cr_{(s)} + Al_2O_{3(s)}$$

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

They both form compounds with variable oxidation states ie

Lead: +2 & +4 and Chromium: +2, +3 & +6

Chromium and Lead in higher oxidation states Cr^{6+} and Pb^{4+} form covalent compounds e.g. $PbCl_4$ and $CrCl_6$

Similarities between the chemistry of Chromium & Aluminium

1. Cr^{3+} and Al^{3+} form complexes with Alkalis.

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

$$Cr(OH)_{3\,(s)} + 3\,OH^-_{(aq)} \longrightarrow [Cr(OH)_6]^{3-}_{(aq)}$$

$$Al^{3+}_{(aq)} + 3\,OH^-_{(aq)} \longrightarrow Al(OH)_{3\,(s)}$$

$$Al(OH)_{3\,(s)} + OH^-_{(aq)} \longrightarrow [Al(OH)_4]^-_{(aq)}$$

2. Oxides and hydroxides of Chromium and Aluminium are amphoteric i.e react with both acids and bases.

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2\,Al(OH)_4^-{}_{(aq)}$$

$$Cr(OH)_{3\,(s)} + 3\,OH^-_{(aq)} \longrightarrow [Cr(OH)_6]^{3-}_{(aq)}$$

$$Al(OH)_{3\,(s)} + OH^-_{(aq)} \longrightarrow [Al(OH)_4]^-_{(aq)}$$

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

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

Test for Cr^{3+} ions in solution

<u>Use of sodium hydroxide solution</u>:

<u>Observation</u>

Grey green precipitate, soluble in excess forming deep green solution.

<u>Equations</u>

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

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

<u>Note:</u>

Chromium (iii) hydroxide is oxidized by hydrogen peroxide solution in an alkaline medium to chromate ions (CrO_4^{2-}) which has a characteristic yellow colour.

Procedure

Sodium hydroxide solution is added drop-wise till excess to a solution containing Cr^{3+} ions followed by a little H_2O_2 and the resultant solution warmed.

Observation:

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

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

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

$$2\,Cr(OH)6^{3-}{}_{(aq)} + 3H_2O_{2\,(aq)} \longrightarrow 2CrO_4^{2-}{}_{(aq)} + 2\,OH^-_{(aq)} + 8H_2O_{(l)}$$

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

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

Observation

A yellow precipitate of lead (ii) chromate is formed.

Equation

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

b) Addition of Barium nitrate or Barium chloride solution.

Observation

A yellow precipitate of barium chromate is formed

Equation

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

c) Addition of silver nitrate solution.

d) Observation

A brick red precipitate of silver (i) chromate is formed.

Equation

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

e) 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.

Use of aqueous ammonia solution:

Observation

Green precipitate slowly dissolves in excess concentrated ammonia solution to form a purple solution.

Equations

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

$$Cr(OH)_{3\ (s)} + 6NH_{3(aq)} \rightarrow [Cr(NH_3)_6]^{3+}{}_{(aq)} + 3\ OH^{-}{}_{(aq)}$$

Use of sodium carbonate / potassium nitrate mixture

Procudure

Fuse the solid suspected to contain Chromium (III) ions with (Na_2CO_3/KNO3) mixture

Observation

A yellow mass of Chromate (CrO_4^{2-}) is formed

MANGANESE

Atomic number is 25

Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

Reactions of manganese

a) Reactions with acids

Manganese being a metal reacts with both dilute hydrochloric and sulphuric acid producing corresponding manganese (ii) salts and hydrogen gas.

$Mn_{(s)} + 2HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + H_{2(g)}$

$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_4(aq) + H_2(g)$

Note

The products when manganese react with dilute nitric acid are not well defined.

b) Reaction with steam

Like magnesium, manganese reacts with hot water to produce manganese (ii) hydroxide and hydrogen gas.

$Mn_{(s)} + H_2O_{(l)} \longrightarrow Mn(OH)_{2(s)} + H_{2(g)}$

c) Reaction with oxygen

Manganese burns in air when heated forming trimanganese tetra oxide

$Mn_{(s)} + O_{2(g)} \longrightarrow Mn_3O_{4(s)}$

Compounds of manganese

Manganese exhibits the following oxidation states; *+2, +3, +4, +5, +6* and *+7*. The *+2* oxidation state being the most stable state because the 3d sub shell is half filled with electrons and therefore energetically stable.

Compound of manganese in the +2 oxidation state

i) Manganese (ii) oxide

On heating either manganese (ii) carbonate or manganese (ii) oxalate, manganese (ii) oxide is produced as a green solid.

$MnCO_{3(s)} \longrightarrow MnO_{(s)} + CO_{2(g)}$

$MnC_2O_{4(s)} \longrightarrow MnO_{(s)} + CO_{(g)} + CO_{2(g)}$

ii) Manganese (ii) hydroxide

On addition of dilute sodium hydroxide solution or aqueous ammonia solution to a solution containing manganese (ii) ion, manganese (ii) hydroxide is formed as a white

precipitate. The precipitate rapidly turns brown due to the aerial oxidation of manganese (ii) oxide formed to manganese hydrated manganese (iv) oxide

$Mn^{2+}{}_{(aq)} + 2\,OH^{-}{}_{(aq)} \longrightarrow Mn(OH)_{2\,(s)}$ *white ppt*

$2Mn\,(OH)_{2\,(s)} + O_{2(g)} \longrightarrow 2MnO_2.H_2O_{(s)}$ *brown ppt*

Note

Manganese (ii) compounds are pink in solid state but in aqueous solution, the pink colour is sometimes too faint to be noticed and so manganese (ii) compounds in aqueous solution may appear colourless.

Compounds of manganese in +4 oxidation state

The most important compound of manganese in this oxidation state is manganese (iv) oxide (manganese dioxide).

It is a dark solid produced on heating manganese (ii) nitrate.

$Mn(NO_3)_{2(s)} \longrightarrow MnO_{2(s)} + NO_{2(g)}$

It is insoluble in water and not attacked by dilute acids.

It reacts with cold concentrated hydrochloric acid to form the complex hexachloro manganate (iv) ion.

$MnO_{2(s)} + 4H^{+}{}_{(aq)} + 6Cl^{-}{}_{(aq)} \longrightarrow MnCl_6^{2-}{}_{(aq)} + 2H_2O_{(l)}$

With hot concentrated hydrochloric acid, manganese (iv) oxide reacts forming chlorine gas as one of the products.

$MnO_{2(s)} + 4HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$

Warm concentrated sulphuric acid reduces manganese (iv) oxide to manganese (ii) sulphate.

$MnO_{2(s)} + H_2SO_{4\,(aq)} \longrightarrow MnSO_{4(aq)} + O_{2(g)} + H_2O_{(l)}$

Note

Manganese (iv) oxide is a powerful oxidizing agent. Some of the oxidizing reactions of manganese (iv) include the following

i) $MnO_{2(s)} + HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$

ii) $MnO_{2(s)} + C_2O_4^{2-}{}_{(aq)} + H^+{}_{(aq)} \longrightarrow Mn^{2+}{}_{(aq)} + 2H_2O_{(l)} + 2CO_{2(g)}$

Compounds of manganese in the +6 oxidation state

Potassium manganate (vi); K_2MnO_4 is the only stable compound of manganese in the +6 oxidation state.

It is a dark green solid prepared on fusing together manganese (iv) oxide with potassium hydroxide in the presence of excess oxygen

$MnO_2(s) + KOH(s) + O_2\ (g) \longrightarrow K_2MnO_4(s) + H_2O(s)$

It can also be prepared by heating manganese (iv) oxide, potassium hydroxide and potassium chlorate.

$MnO_{2(s)} + 6KOH_{(aq)} + KClO_{3(aq)} \longrightarrow K_2MnO_{4(s)} + KCl_{(aq)} + 3H_2O_{(l)}$

Potassium manganate (vi) is also a powerful oxidizing agent.

Behavior of potassium manganate (VI) in

a) Acidic medium

$MnO_4^{2-}{}_{(aq)} + H^+{}_{(aq)} \longrightarrow 2MnO_4^-{}_{(aq)} + MnO_{2(s)} + 2H_2O_{(l)}$

b) Neutral medium

$3K_2MnO_{4(s)} + 2H_2O_{(l)} \longrightarrow KMnO_{4(s)} + MnO_{2(s)} + 4KOH_{(aq)}$

Compounds of manganese in the +7 oxidation state

Potassium manganate (vii) (potassium permanganate) is the most important compound of manganese in the +7 oxidation state.

Potassium permanganate is a powerful oxidizing agent and although not a primary standard, it's commonly used in volumetric analysis because of the following;

1) End points involving manganate (vii) titrations do not need indicators. The persistence of the intense purple colour of the permanganate solution when added from a burette indicates the end point of the titration has been reached.

2) Permanganate titrations have sharp end points

3) Potassium permanganate is fairly soluble in water.

4) Potassium manganate (vii) has a fairly high formula mass and this reduces errors due to weighing inefficiencies.

Note

1) Potassium manganate is not a primary standard because it aqueous solution on standing is reduces to manganese (iv) oxide which appears as brown solid.

2) In acidic medium in the presence of an oxidizing agent, manganate (vii) ions react as shown by the equation below

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

3) The purple colour of the manganate (vii) solution turns colourless due to the formation of manganese (ii) ions.

4) Only dilute sulphuric acid is used to acidify the solution.

5) Dilute hydrochloric acid is not used because it is oxidizes by the manganate (vii) solution forming chlorine gas which is an interference to the desired reaction

$$2KMnO_{4\,(aq)} + 16HCl_{(aq)} \longrightarrow 2MnCl_{2\,(aq)} + 2KCl_{(aq)} + 5Cl_{2(g)} + 8H_2O_{(l)}$$

6) Dilute nitric acid is not used because itself like potassium manganate (vii) is an oxidizing agent and therefore would interfere with the desired reaction.

7) Some of the oxidizing properties of manganate (vii) ions (MnO_4^-) in acidic medium include:

a) $2MnO_4^-{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} + 16\,H^+{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)}$

b) $MnO_4^-{}_{(aq)} + 5Fe^{2+}{}_{(aq)} + 8H^+{}_{(aq)} \longrightarrow 5Fe^{3+}{}_{(aq)} + Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

c) $2MnO_4^-{}_{(aq)} + 5H_2O_{2(aq)} + 6H^+{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$

d) $2MnO_4^-{}_{(aq)} + 5Sn^{2+}{}_{(aq)} + 16H^+{}_{(aq)} \longrightarrow 5Sn^{4+}{}_{(aq)} + 2\,Mn^{2+}{}_{(aq)} + 8H_2O_{(l)}$

Revision questions

a) Write the electronic configuration of the following species (atomic number= 25):

i. *Mn*

ii. Mn^{2+}

iii. Mn^{3+}

iv. Mn^{7+}

b) State the most stable oxidation state of Manganese. Give a reason for your answer.

c) State the possible oxidation states of manganese.

d) Explain why manganese shows variable oxidation states.

e) Aqueous sodium hydroxide was added drop wise to a solution containing Mn^{2+},

State what was observed and write equation for the reaction that took place.

f) Give a formula of a compound or ion containing Manganese in an oxidation state of +7 oxidation state?

g) Write equation to show the reduction of MnO_4^- in :

i. Alkaline medium.

ii. Acidic medium.

h) Discuss the chemistry of manganese and magnesium showing similarities.

Answer

a)

i) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

iii) $1s^2 2s^2 2p^6 3s^2 3p^6$

b) The most stable oxidation state is +2. This is because after using the 4s-electrons, a half filled 3d -orbital that is stable is left.

c) +2, +3, +4, +5, +6, +7.

Acidity of the oxide of manganese increases with the increasing oxidation state.

d) The variable oxidation state of manganese is due to the fact that both the 4s and the 3d-electrons take part in bond formation.

This is because electrons are being removed from energetically similar 4s and 3d-orbitals.

For +2 oxidation states, only the 4s-electrons are utilized for bond formation, forming stable Mn^{2+}. For higher oxidation states, both the 4s and 3d- electrons are utilized.

e) Observation:

White precipitate insoluble in excess turns brown on standing due to aerial oxidation to Manganese iv oxide.

Equation:

$$Mn^{2+}{}_{(aq)} + 2\,OH^{-}{}_{(aq)} \longrightarrow Mn(OH)_{2\,(s)}\ \textit{white ppt}$$

$$2Mn(OH)_{2\,(s)} + O_{2(g)} \longrightarrow 2MnO_2.H_2O_{(s)}\ \textit{brown ppt}$$

Note

A similar observation & reactions occur on addition of aqueous ammonia solution to a solution containing Manganese (ii) ions.

f) MnO_4^-

Manganese $1s^22s^22p^63s^23p^64s^23d^5$ shows an oxidation state of +7 by using all the 4s and 3d- electrons in the bond formation because they are energetically similar.

g) In alkaline condition, the change in oxidation state is from $^{+}7$ to $^{+}4$ since potassium manganate (vii) is a mild oxidizing agent in alkaline medium

$$MnO_4^-{}_{(aq)} + 2H_2O_{(l)} + 3e \longrightarrow MnO_{2\,(s)} + 4OH^-{}_{(aq)}$$

Or

$$MnO_4^-{}_{(aq)} + 4H^+{}_{(aq)} + 3e \longrightarrow MnO_{2(s)} + 2H_2O_{(l)}$$

In acidic medium, the reaction is as shown below.

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

Note

$KMnO_4$ has wide applications in the laboratory including the following:

- Being used as indicator in volumetric analysis titrations involving its solution.
- To test for reducing agents e.g. sulphur dioxide.
- Estimating iron (ii) salts and oxalates.
- Preparation of gases e.g. chlorine gas is liberated when Conc. hydrochloric acid is reacted with it.

Hydrochloric acid is not used to acidify $KMnO_4$ during titration because potassium permanganate solution is a very strong oxidizing agent, oxidizes chloride ions from hydrochloric acid to chlorine which interferes with the desired reaction.

$$2KMnO_{4\,(aq)} + 16HCl_{(aq)} \longrightarrow 5Cl_{2(g)} + 2KCl_{(aq)} + 2MnCl_{2(aq)} + 8H_2O_{(l)}$$

h) They both react with chlorine to form chloride when heated.

$$Mn_{(s)} + Cl_{2(g)} \rightarrow MnCl_{2(s)}$$

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

They both react directly with nitrogen to form similar nitrides

$$3Mn_{(s)} + N_{2(g)} \rightarrow Mn_3N_{2(s)}.$$

$$3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$$

They both react with dilute hydrochloric acid to liberate hydrogen gas.

$$Mn_{(s)} + 2HCl_{(aq)} \rightarrow MnCl_{2(aq)} + H_{2(g)}.$$

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

Manganese reacts with hot water to form oxide. Magnesium reacts with steam in a similar way.

$$Mn_{(s)} + H_2O_{(l)} \rightarrow MnO_{(s)} + H_{2(g)}$$

$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$$

Note:

Confirmatory test of Manganese, Mn^{2+} ions in solution

Procedure

To solid manganese (II) salt is added concentrated nitric acid and little solid lead (IV) oxide or sodium bismuthate solution and the mixture

boiled.

Observation

A purple solution forms due to the formation of manganate (vii) ions

Equations

$2Mn^{2+}_{(aq)} + 5\ BiO_3^-{}_{(aq)} + 14H^+_{(aq)} \rightarrow 2MnO_4^-{}_{(aq)} + 5Bi^{3+}_{(aq)} + 7H_2O_{(I)}$

$2Mn^{2+}_{(aq)} + 5PbO_{2(s)} + 4H^+_{(aq)} \rightarrow 2MnO_4^-{}_{(aq)} + 5Pb^{2+}_{(aq)} + 2H_20_{(1)}$

IRON

Ores of iron:

- *Haematite ,* ***Fe_2O_3***
- *Magnetite ,* ***Fe_3O_4***
- *Iron Pyrite ,* ***FeS_2***
- *Siderite ,* ***$FeCO_3$***

The 1st two ores are fed directly into a blast furnace but the last two must first be roasted in air to convert them to stable iron (iii) oxide before feeding them into the blast furnace. i.e.

$4FeS_{2(s)} + 11\ O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$

$4FeCO_{3(s)} + O2_{(g)} \rightarrow 2Fe_2O_{3(s)} + 4CO_{2(g)}$

Extraction of iron

Iron is commonly extracted from its ore called haematite (Fe_2O_3) using a blast furnace

The raw materials used in the extraction are:

1) *The ore, Haematite*
2) *Coke*
3) *Limestone(calcium carbonate)*

4) *Hot air*

The hot blast of air enters the blast furnace through narrow pipes called tuyeres located at the lower part of the furnace.

The other materials are fed into the furnace from the top.

Reactions taking place in the blast furnace

In the presence of hot air coke burns to produce carbon dioxide gas

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

As the carbon dioxide ascends, it reacts with unburnt coke to form carbon monoxide

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

The carbon monoxide produced reduces the ore to iron.

$Fe_2O_{3(s)} + 3CO_{(g)} \rightleftharpoons 2Fe_{(l)} + 3CO_{2(g)}$

The role of the limestone is to remove impurities like silica (SiO_2)

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

The quick lime then combines with silica and alumina present as impurities to form slag.

$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(l)}$

$CaO_{(s)} + Al_2O_{3(s)} \rightarrow CaAl_2O_{4(l)}$

Molten iron and slag both sink to the bottom of the furnace and they can be tapped off separately. The molten iron at the bottom is covered by the slag to prevent oxidation.

The molten iron solidifies on cooling to form PIG iron.

Properties of pig iron:

- Low melting point.
- Impure i.e. contain impurities such as carbon, silicon, sulphur, etc.

Pig iron can be used in making gas stove, drainage pipes, bunsen burner bases, boiler plates etc

Purification of pig iron

The Bessemer process:

This involves pouring the molten iron into a large tab called the converter and air is blown into it to oxidize the impurities such as carbon, sulphur and phosphorus to their gaseous oxides.

Reactions of iron

a) With air

Iron combines with oxygen when heated to form black solid of tri-iron tetra oxide.

$3Fe_{(s)} + 2\ O_{2\ (g)} \rightarrow Fe_3O_{4(s)}$

Iron reacts with moist cold air to form brown hydrated iron (iii) oxide or rust.

$2Fe_{(s)} + 6H_2O_{(l)} + 3\ O_{2\ (g)} \rightarrow 2Fe_2O_3.3H_2O_{(s)}$

How rusting occurs:

Rusting is an electrochemical process which takes place when different parts of iron act as anode and cathode.

At the cathodic region:

$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e$

At the anodic region:

$2\ H_2O_{(l)} + O_{2\ (g)} + 4e \rightleftharpoons 4OH^-_{(aq)}$

If the cathodic and anodic areas are close enough, iron (ii) hydroxide is formed.

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

Moist air then oxidizes the iron (ii) hydroxide to rust.

$4Fe\ (OH)_{2(s)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 2Fe_2O_3.3H_2O_{(s)}$

Prevention of rusting

a. Painting

b. Greasing

c. Galvanizing (coating with zinc)

b) With water

Heated iron reacts with steam to form black tri-iron tetra oxide.

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

c) With acid.

Iron reacts with dilute acids (HCl & H_2SO_4) to form hydrogen gas and iron (ii) salts.

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)}$$

$$Fe_{(s)} + H_2SO_{4(aq)} \rightarrow FeSO_{4(aq)} + H_{2(g)}$$

Hot conc. sulphuric acid oxidizes iron to iron (iii) sulphate, sulphur dioxide and water.

$$2Fe_{(s)} + 6H_2SO_{4(aq)} \rightarrow Fe_2(SO_4)_{3(aq)} + 3SO_{2(g)} + 6H_2O_{(aq)}$$

d) With halogens.

Heated iron reacts with dry chlorine gas to form iron (iii) chloride.

$$2Fe_{(s)} + 3Cl_{2(g)} \rightarrow FeCl_{3(s)}$$

Compounds of iron

+2 oxidation state

In aqueous solution exists as $[Fe(H_2O)_6]^{2+}$ which is a green solution. It undergoes hydrolysis making the resultant solution acidic.

Iron (ii) hydroxide

It's a green ppt formed when sodium hydroxide solution is added drop wise to a solution of Fe^{2+} solution. The ppt is insoluble in excess and turns brown due to aerial oxidation on exposure to air.

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

$$4Fe(OH)_{2(s)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow 2Fe_2O_3.3H_2O_{(s)}$$

NB:

Similar reaction occurs on addition of ammonia solution to aqueous Fe^{2+} solution

Hydrated iron (ii) sulphate. $FeSO_4.7H_2O$

It's prepared by heating iron fillings with dilute sulphuric acid and crystallizing the salt from solution.

During the crystallization process, hydrated iron (ii) sulphate forms as green crystals.

$$Fe_{(s)} + H_2SO_{4(aq)} \longrightarrow FeSO_{4(aq)} + H_{2(g)}$$

Action of heat on hydrated iron (ii) sulphate

On gentle heating

$$FeSO_4.7H_2O_{(s)} \longrightarrow FeSO_{4(s)} + 7H_2O_{(g)}$$

On further heating.

$$2FeSO_{4(s)} \longrightarrow Fe_2O_{3(s)} + SO_{3(g)} + SO_{2(g)}$$

White acidic fumes

If conc. nitric acid is added to iron (ii) sulphate, the green solution turns to yellow/ brown due to formation of iron (iii) ions.

Ammonium Ferrous Sulphate (Ammonium Iron (ii) sulphate) $(NH_4)_2SO_4.FeSO_4.6H_2O$

By mixing equimolar concentrated solutions of iron (ii) sulphate and ammonium sulphate, ammonium ferrous sulphate is formed.

It is a green double salt preferred to iron (ii) sulphate in volumetric analysis because it is not efflorescent and also not easily oxidized.

+3 oxidation state

This is the most stable oxidation state of iron.

The soluble salts in this oxidation state exist as $[Fe(H_2O)_6]^{3+}$ and undergo hydrolysis in water making resultant solution acidic.

e.g. a solution of iron (iii) chloride turns blue litmus red.

The Fe^{3+} ion is small and highly charged. It undergoes hydrolysis in aqueous solution to release hydrogen ions or hydroxonium ions which make the resultant solution acidic.

$FeCl_{3(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 3Cl^{-}{}_{(aq)}$

$Fe^{3+}{}_{(aq)} + 6H_2O_{(l)} \rightarrow [Fe(H_2O)_6]^{3+}{}_{(aq)}$

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

Brown ppt

Or

$[Fe(H_2O)_6]^{3+}{}_{(aq)} \rightleftharpoons [Fe(H_2O)_3(OH)_3]_{(s)} + 3H^{+}{}_{(aq)}$

On addition of zinc powder to a brown/ yellow solution of iron (iii), the color of the solution changes to green.

$2Fe^{3+}{}_{(aq)} + Zn_{(s)} \rightarrow 2Fe^{2+}{}_{(aq)} + Zn^{2+}{}_{(aq)}$

The resultant solution can now be titrated with acidified solution of standard potassium permanganate.

$MnO_4{}^{-}{}_{(aq)} + 8H^{+}{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$

On bubbling hydrogen sulphide gas to a solution containing Fe^{3+} ion, the color of the solution changes from yellow to green with formation of a yellow solid.

$H_2S_{(g)} + 2Fe^{3+}{}_{(aq)} \rightarrow 2H^{+}{}_{(aq)} + 2Fe^{2+}{}_{(aq)} + S_{(s)}$

Similarities in the chemistry of zinc and iron

1) Both metals when heated (red hot) react with steam to form oxide and hydrogen gas.
   $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

   $Zn_{(s)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}$

2) Both react with dilute acid (HCl & H_2SO_4) to liberate hydrogen gas.

   $Fe_{(s)} + H_2SO_{4(aq)} \rightarrow FeSO_{4(aq)} + H_{2(g)}$
   $Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$

3) Both metal when heated react with oxygen to form oxide.

$3Fe_{(s)} + 2\,O_{2(g)} \rightarrow Fe_3O_{4(s)}$
$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$

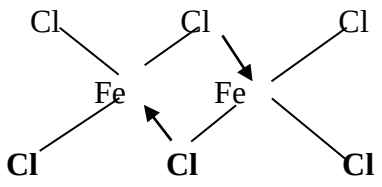
4) Both metals when heated react with chlorine to form chloride.
$2Fe_{(s)} + 3Cl_{2(g)} \rightarrow 2FeCl_{3(s)}$
$Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)}$

5) 5)Both elements react with sulphur to form sulphide.
$Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$
$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$

Differences in the chemistry of Zinc & Iron

1) Zn dissolves in conc. alkalis forming hydrogen gas but iron does not react with alkalis.
$Zn_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + H_{2(g)}$
2) Zn shows a single valency of +2 while iron exhibits variable valencies of *+2,+3* and *+6*
3) Zn forms compounds that are white in color where as Fe forms compounds which are colored.
Fe^{2+} *-green*
Fe^{3+} *-brown*
4) Iron is paramagnetic(due to unpaired electrons in the 3d-subshell) while Zn is diamagnetic(due to paired electrons in its 3d-subshell)

5) Fe forms dimeric chloride, Fe_2Cl_6.



6) Zinc does not react with cold moist air. Iron reacts with moist air to form hydrated iron (iii) oxide (rust).

Test for Iron (ii) and Iron (iii) ions in aqueous solution

a) <u>Test for Ferrous ions (Fe^{2+})</u>
<u>Use of sodium hydroxide solution / aqueous ammonia solution</u>
<u>Procedure</u>
To the solution containing the unknown cation is added dilute sodium hydroxide solution or aqueous ammonia dropwise until in excess.

Observation

In the presence of Iron (ii) ions, a green precipitate of Iron (ii) hydroxide is formed. The precipitate turns brown due to aerial oxidation to iron (iii) hydroxide.

Equation

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

Use of Potassium hexacyanoferrate (iii) solution

Procedure

To the solution containing the unknown cation is added potassium hexacyanoferrate (iii) solution.

Observation

A dark blue precipitate (turnbull's blue) is formed.

Equation

$K^{+}_{(aq)} + [Fe(CN)_6]^{3-}_{(aq)} + Fe^{2+}_{(aq)} \longrightarrow K[Fe(Fe(CN)_6]_{(s)}$

Test for Iron (iii) ions in solution

Use of sodium hydroxide solution/ aqueous ammonia solution

Procedure

To the solution containing the unknown cation is added dilute sodium hydroxide or aqueous ammonia solution dropwise until in excess.

Observation

A reddish brown precipitate of iron (iii) hydroxide is produced. The precipitate is insoluble in excess sodium hydroxide/ aqueous ammonia.

Equation

$Fe^{2+}_{(aq)} + 3OH^{-}_{(aq)} \longrightarrow Fe(OH)_{3(s)}$

Use of potassium hexacyanoferrate (ii) solution

Addition of a few drops of potassium hexacyanoferrate (ii) solution to solution containing iron (iii) ions produces a dark blue precipitate (Prussian blue). Equation

$K^{+}_{(aq)} + [Fe(CN)_4]^{4-}_{(aq)} + Fe^{3+}_{(aq)} \longrightarrow K[Fe(Fe(CN)_6]_{(s)}$

Use of potassium thiocyanate solution

Procedure

Addtidion of potassium thiocyanate solution to a solution containing Fe^{3+} ion s produces a blood red coloration of thiocyanato penta aqua iron(III)complex ion.

$$[Fe(H_2O)_6]^{3+}_{(aq)} + SCN^{-}_{(aq)} \longrightarrow [Fe(H_2O)_5SCN]^{2+}_{(aq)} + H_2O_{(l)}$$

Question.

State the similarities in the chemistry of zinc & magnesium.

COBALT

Reaction of Cobalt (II) ion, Co^{2+}

The +2 oxidation state is the most stable for simple cobalt salts.

Cobalt (ii) compounds are colored pink. The simplest ion that cobalt forms in solution is the hexa aqua cobalt (II) ion - $[Co(H_2O)_6]^{2+}$.*which is pink in colour*

A ligand exchange reaction involving chloride ions

If you add concentrated hydrochloric acid to a solution containing hexa aqua cobalt(II) ions, the solution turns from its original pink colour to a rich blue. The six water molecules are replaced by four chloride ions.

The reaction taking place is reversible.

$$Co(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

If you add water to the blue solution, it turns back to the pink colour due to the formation of hydrated cobalt (ii) ions.

a) <u>Reaction of cobalt (ii) ions with sodium hydroxide solution</u>
A blue precipitate formed insoluble in excess and turns pink on standing
$Co^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Co(OH)_{2(s)}$

<u>With sodium hydroxide solution and hydrogen peroxide</u>
Rather than relying on oxidation by the air, you can add an oxidizing agent such as hydrogen peroxide
You get the cobalt (II) hydroxide complex when you add the sodium hydroxide solution.
Addition of hydrogen peroxide produces lots of bubbles of oxygen and a dark chocolate brown precipitate. The final precipitate contains cobalt in the +3 oxidation state.
$4Co(OH)_{2\,(s)} + 2H_2O_{2\,(aq)} \longrightarrow 4Co(OH)_{3\,(s)}$

b) <u>Reaction of cobalt (ii) ions with ammonia solution</u>
A blue precipitate formed which dissolves in excess to form a brown solution and turns to a deep red -brown solution on standing in air.
$Co^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Co(OH)_{2(s)}$
$Co(OH)_{2(s)} + 6NH_{3(aq)} \rightarrow Co(NH_3)_6^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$
$Co(NH_3)_6^{2+}{}_{(aq)} \rightarrow Co(NH_3)_6^{3+}{}_{(aq)} + e$

c) <u>With ammonia solution and hydrogen peroxide</u>

Rather than relying on oxidation by the air, you can add an oxidizing agent such as hydrogen peroxide
The reaction with ammonia solution followed by hydrogen peroxide produces the same dark reddish-brown solution as before only that the reaction is faster this time. The equation for the oxidation of the ammine complex is:

$$2Co(NH_3)_6^{2+} + H_2O_2(aq) \longrightarrow 2Co(NH_3)_6^{3+}{}_{(aq)} + 2OH^-{}_{(aq)}$$

NICKEL

Test for Nickel (II) Ion, Ni^{2+} in solution

a) Use of of dilute sodium hydroxide solution
A green precipitate insoluble in excess formed.
$Ni^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Ni(OH)_{2(s)}$

b) Use of aqueous ammonia Solution
A green precipitate formed which dissolves in excess to form a blue solution
$Ni^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Ni(OH)_{2(s)}$
$Ni(OH)_{2(s)} + 6NH_{3(aq)} \rightarrow (Ni(NH_3)_6^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$

Note
The initial pale green precipitate of $Ni(OH)_2$ is frequently not seen if Ni^{2+} solution is dilute.

c) Use of dimethylglyoxime
Procedure
To the solution containing Ni^{2+} is 1st added aqueous ammonia solution drop-wise until in excess followed by a drop of dimethylglyoxime solution.
Observation
A green ppt soluble in excess ammonia forming a blue solution. On addition of dimethylglyoxime, a red precipitate of nickel dimethylglyoxime complex is formed .

COPPER

Atomic number is 29

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Ores of copper

1. copper pyrite $CuFeS_2$

2. malachite $CuCO_3.Cu(OH)_2$

Extraction of copper

Copper is commonly extracted from its ore called copper pyrite.

The ore is 1st crushed to powder form. The finely divided ore is then mixed with water and frothing agent such as pine oil is added. The earthly materials sink to the bottom because of their high density whereas the ore particles float on top from where they are removed, washed and dried.

The ore is then roasted to convert the copper pyrite to copper (i) sulphide, iron(ii) oxide and sulphur dioxide.

$2CuFeS_{2(s)} + 4O_{2(g)} \rightarrow Cu_2S_{(s)} + 2FeO_{(s)} + 3SO_{2(g)}$

The solid product is transferred into a blast furnace and silica added.

On strong heating, the iron(ii)oxide reacts with silica to form slag.

$FeO_{(s)} + SiO_{2(s)} \rightarrow FeSiO_{3(l)}$

The copper (i) sulphide reacts with air forming copper (i) oxide.

$2Cu_2S_{(s)} + 3O_{2(g)} \rightarrow 2Cu_2O_{(s)} + 2SO_{2(g)}$

The copper (i)oxide produced and the unroasted copper (i) sulphide react in the heat of the blast furnace with limited air supply to form copper.

$2Cu_2O_{(s)} + Cu_2S_{(s)} \rightarrow 6Cu_{(l)} + SO_{2(g)}$

The copper formed solidifies on cooling and is called blister copper and contains impurities. The last process in the extraction is purification of blister copper.

Extraction from malachite

Concentration process

The ore is ground to powder. The finely divided ore particles is mixed with water and frothing agent such as pine oil and shaken for a while.

The earthly materials because of their high density sink to the bottom whereas the ore particles because of their low density float on the surface, where they are removed, washed and dried.

The ore is roasted to form copper (ii) oxide.

$CuCO_3.Cu\ (OH)_{2(s)} \rightarrow 2CuO_{(s)} + CO_{2(g)} + H_{2(g)}$

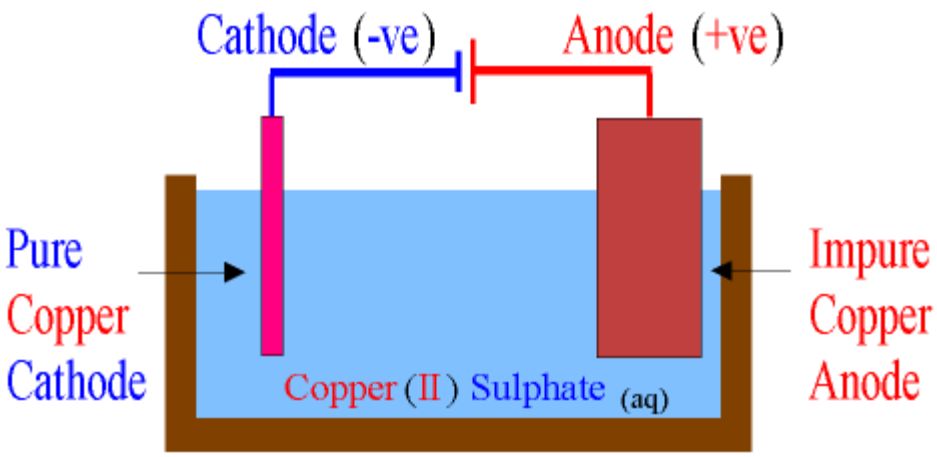
The copper(ii) oxide is reduced with carbon on heating to copper.

$CuO_{(s)} + C_{(s)} \rightarrow Cu_{(s)} + CO_{2(g)}$

The copper formed is then purified by electrolysis.

<u>Purification of Copper</u>

–Electrolysis



- The anode is a block of made of the impure copper to be purified.
- The cathode is a thin piece of pure copper
- The electrolyte is copper (ii) sulphate solution.
- When electricity is passed through the cell,

At the Anode

Copper is dissolved by oxidation i.e Cu^{2+} ions go into solution.

- $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e$

At the cathode,

- copper is deposited by reduction.
- $Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$
- As copper ions move from the anode to the cathode the anode gets smaller as the cathode gets bigger

Uses of copper

Amongst other things copper is used for:

- Electrical wiring. It is a very good conductor of electricity and is easily drawn out into wires.
- Domestic plumbing. It doesn't react with water, and is easily bent into shape.
- Boilers and heat exchangers. It is a good conductor of heat and doesn't react with water.
- Making brass. Brass is a copper-zinc alloy. Alloying produces a metal harder than either copper or zinc individually.
- Bronze is another
- Copper alloy - this time with tin.
- Coinage. Copper-colored coins, "silver" coins are also copper alloys - this time with nickel. These are known as cupronickel alloys.
- UK pound coins and the gold-colored bits of euro coins are copper-zinc-nickel alloys.

Reactions of copper

1) With air
   Copper reacts with moist air to form a green outer layer of copper (ii) carbonate (protective layer).

Heated copper reacts with oxygen enriched air (below 800 ^oC) to form black copper (ii) oxide.

$2Cu_{(s)} + O_{2(g)} \rightarrow 2CuO_{(s)}$

At very high temperature> 800 ^oC, copper reacts with oxygen to form copper (i) oxide.

$4Cu_{(s)} + O_{2(g)} \rightarrow 2Cu_2O_{(s)}$

2) <u>With halogens</u>.
   Heated copper reacts with halogen to form copper (ii) halide.
   $Cu_{(s)} + Cl_{2(g)} \rightarrow CuCl_{2(s)}$
   However copper reacts with iodine to form copper (i) iodide.
3) <u>With sulphur.</u>
   When heated, copper forms a sulphide .
   $Cu_{(s)} + S_{(s)} \rightarrow CuS_{(s)}$

4) <u>With acids</u>
   a. Dilute nitric acid reacts with copper to form copper (ii) nitrate, nitrogen monoxide and water.
      $3Cu_{(s)} + 8HNO_{3\,(aq)} \rightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$

   b. Copper reacts with concentrated nitric acid to form copper (ii) nitrate, nitrogen dioxide gas and water.

      $Cu_{(s)} + 4HNO_{3\,(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

   c. Copper reacts with concentrated sulphuric acid to form copper (ii) sulphate, sulphur dioxide and water.
      $Cu_{(s)} + 2H_2SO_{4\,(aq)} \rightarrow CuSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$

Compounds of copper

Copper shows 2 oxidation states of +1 and +2, however compounds in +1 oxidation state are unstable.

Compounds in +2 oxidation states

This is the most stable oxidation state of copper and in aqueous solution exists as $[Cu(H_2O)_4]^{2+}$ which is a blue solution.

It slowly undergoes hydrolysis forming acidic solution.

$$[Cu(H_2O)_4]^{2+}{}_{(aq)} \rightleftharpoons [Cu(H_2O)_3OH]^{+}{}_{(aq)} + H^{+}{}_{(aq)}$$

1) <u>Copper (ii) hydroxide</u>

It's a blue ppt formed when aqueous sodium hydroxide is added to copper (ii) ions.

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

Copper (ii) hydroxide does not dissolve in excess sodium hydroxide. However dissolves in excess ammonia solution to form a deep blue solution.

$$Cu(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]^{2+}{}_{(aq)} + 2OH^{-}(aq)$$

Tetraammine copper (ii) ions

2) <u>Copper (ii) chloride.</u>

It's prepared by adding a stream of dry chlorine gas over heated copper metal.

$$Cu_{(s)} + Cl_{2(g)} \rightarrow CuCl_{2(s)}$$

In aqueous solution, it exists as $[Cu(H_2O)_4]^{2+}$.

It slowly undergoes hydrolysis forming acidic solution.

$$[Cu(H_2O)_4]^{2+}{}_{(aq)} \rightleftharpoons [Cu(H_2O)_3OH]^{+}{}_{(aq)} + H^{+}{}_{(aq)}$$

Copper (ii) chloride dissolves in conc. hydrochloride acid to form a yellow solution of tetrachlorocuprate (ii) ions $[CuCl_4]^{2-}$

<u>Note:</u>

A complex ion may undergo ligand exchange whereby all its ligands are replaced by a different ligand which is more willing to donate the pair of electrons more readily. Altering a ligand around a central metal ion brings about a marked color change.

E.g. $[Cu(H_2O)_6]^{2+}$

$$[CuCl_4]^{2-} \xleftarrow{\text{excess conc. HCl}} [Cu(H_2O)_4]^{2+} \xrightarrow{\text{excess ammonia}} [Cu(NH_3)_4]^{2+}$$

Yellow *Blue* *Deep blue*

Determination of copper (ii) ions in copper (ii) salts

<u>Method1</u>

Applicable to any soluble salt of copper.

(starting from copper ore, dissolve the ore in dilute sulphuric acid)

Procedure:

To a solution containing copper (ii) ions is added excess potassium iodide, a white precipitate of copper(i) iodide is formed which is stained brown by the liberated iodine.

$$2Cu^{2+}_{(aq)} + 4I^{-}_{(aq)} \rightarrow Cu_2I_{2(s)} + I_{2(aq)}$$

White ppt *brown soln*

The amount of iodine liberated is then determined by titrating the resultant solution with a standard solution of sodium thiosulphate using starch as indicator.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$$

The volume of thiosulphate solution used is noted.

Treatment of results

The overall equation of reaction is obtained by adding the two equations above:

$$2Cu^{2+}_{(aq)} + 2S_2O_3^{2-}{}_{(aq)}\, 2I^{-}_{(aq)} \longrightarrow Cu_2I_{2(s)} + S_4O_6^{2-}{}_{(aq)}$$

2 moles of thiosulphate ions react with 2 moles of Cu^{2+} ions.

Thus knowing the moles of thiosulphate ions that reacted, that of copper ions present in the solution can be determined.

Method 2

This method applies to copper (ii) iodate only $Cu(IO_3)_2$

i) $Cu(IO_3)_{2(s)} + aq \longrightarrow Cu^{2+}_{(aq)} + 2IO_3^{-}{}_{(aq)}$

ii) $IO_3^{-}{}_{(aq)} + 5I^{-}_{(aq)} + 6H^{+}_{(aq)} \longrightarrow 3I_{2(aq)} + 3H_2O_{(l)}$

iii) $I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^{-}_{(aq)}$

To a solution containing copper (ii) iodate is added excess potassium iodide solution followed by dilute sulphuric acid.

Iodine is liberated according to the equations above. The liberated iodine is then titrated with a standard solution of sodium thiosulphate using starch as indicator. The volume of thiosulphate used is noted.

Test for Copper(II) ions.

Use of Sodium Hydroxide solution

Procedure:

To the solution containing the cation is added sodium hydroxide dropwise till in excess.

Observation

A blue precipitate of $Cu(OH)_2$ insoluble in excess sodium hydroxide is formed.

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

The precipitate turns black on heating due to the formation of copper(II)oxide.

Use of aqueous ammonia solution

Observation

A blue precipitate of copper(II)hydroxide soluble giving a deep blue solution Tetraammine copper(II)ions complex.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+}_{(aq)}$$

Use of potassium Iodide Solution

Procedure

To the solution containing copper(II)ions is added Potassium Iodide Solution.

Observation:

A white precipitate of copper (I) iodide and a brown solution of Iodine is produced.

$$2Cu^{2+}_{(aq)} + 4I^{-} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$$

Use of Potassium hexacyanoferrate(II) solution

Procedure

To the solution containing copper (II) ions is added Potassium hexacyanoferrate(II) Solution.

A brown precipitate of copper hexacyanoferrate(II)

$$Cu^{2+}_{(aq)} + [Fe(CN)_6]^{4-}(aq) \longrightarrow Cu_2[Fe(CN)_6]_{(s)}$$

ZINC AND ITS COMPOUNDS

Atomic number is 30.

Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Ores of Zinc

- *Zinc blende :ZnS*
- *Zinc calamine:* $ZnCO_3$

Extraction process from sulphide ore

The ore contains traces of lead sulphide and silica as impurities which should be removed.

Concentration of the ore

The ore is first crushed and mixed with water and oil (a frothing agent) so as to remove the unwanted earthly materials.

The oil wets the sulphide particles and the water wets the impurities.

Air is then blown through the mixture producing froth. The oiled sulphide particles float on the surface while the impurities sink to the bottom. The ore is collected, washed and dried.

Roasting

The concentrated ore is then heated strongly in air to form zinc oxide.

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$

Reduction

Zinc oxide, limestone ($CaCO_3$) and excess coke are then heated in a blast furnace.

Limestone decomposes into calcium oxide and carbon dioxide.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

The calcium oxide reacts with silica, one of the impurities to form calcium silicate (slag).

$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(l)}$

Coke burns to carbon dioxide, which is reduced by unburnt coke to carbon monoxide. The carbon monoxide reduces zinc oxide to zinc.

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

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

$ZnO_{(s)} + CO_{(g)} \rightarrow Zn_{(l)} + CO_{2\,(g)}$

The slag sinks to the bottom and can be removed whereas the zinc produced leaves as vapour at the top of the blast furnace where its cooled and allowed to solidify.

Reactions of zinc

a) <u>With air</u>

On exposure to air, zinc develops a thin layer of zinc oxide. This layer prevents further reaction with the oxygen present in air.

Zinc burns in air (oxygen) to form zinc oxide.

$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$

(Yellow when hot and white on cooling)

b) <u>With water</u>

Zinc (red hot) reacts with steam to form zinc oxide and hydrogen gas.

$Zn_{(s)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}$

c) <u>With acid</u>

Zinc reacts with both dilute and conc. hydrochloric acid forming salt and hydrogen gas.

$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

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

$Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$

d) <u>Reaction of zinc with conc. H_2SO_4</u>

Produces zinc sulphate, sulphur dioxide and water as the products.

$Zn_{(s)} + 2H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + 2\,H_2O_{(aq)} + SO_{2(g)}$

NB:

The products for the reaction with nitric acid (both dilute and conc.) are not easily defined.

e) With alkalis

Zinc reacts with aqueous alkalis to form zincates' complex and hydrogen gas.

$Zn_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + H_{2(g)}$

Compounds of zinc

1) <u>Zinc hydroxide</u>

It is prepared as a white precipitate on addition of a little sodium hydroxide or aqueous ammonia to a solution containing zinc ions.

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

White ppt

The hydroxide is amphoteric. It dissolves in excess sodium hydroxide to form sodium zincates' complex.

$Zn(OH)_{2(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)}$

In aqueous ammonia, zinc hydroxide dissolves forming a colorless solution of tetra amine zinc ion.

$Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow Zn(NH_3)_4^{2+}{}_{(aq)} + 2OH^-_{(aq)}$

2) <u>Zinc Sulphide</u>

This is prepared as a white ppt on passing hydrogen sulphide through a solution of zinc ions.

When H_2S gas is passed through a solution of a metallic salt, a metallic sulphide is formed but if the H_2S is passed through an acidic solution of a metallic salt, the sulphide may not be formed.

Explanation:

$H_2S_{(g)} + aq \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$

$Zn^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow ZnS_{(s)}$

If before bubbling hydrogen sulphide the solution is acidified, the excess H+ ions present suppresses the formation of sulphide ions in 1st equation above and therefore the concentration of sulphide ions will be too low to precipitate zinc sulphide.

<u>Note</u>

Aqueous solution of zinc chloride is acidic due to hydrolysis of $[Zn(H_2O)_6]^{2+}$

$ZnCl_{2(s)} + 6H_2O_{(l)} \rightarrow [Zn(H_2O)_6]^{2+}{}_{(aq)} + 2Cl^-_{(aq)}$

$[Zn(H_2O)_6]^{2+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Zn(H_2O)_5OH]^+{}_{(aq)} + H_3O^+{}_{(aq)},$

Test for zinc ions

1) Addition of aqueous sodium hydroxide drop wise to a solution of zinc ions produces a white ppt which dissolves in excess alkali to form a colourless solution.

$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)}$ *White ppt*

$Zn(OH)_{2(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)}$ *colorless solution*

2) Addition of ammonia solution drop wise to a solution of zinc ions produces a white ppt soluble in excess to form a colorless solution.
3) $Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)}$

   $Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow Zn(NH_3)_4^{2+}{}_{(aq)} + 2OH^-_{(aq)}$

4) Addition of potassium ferrocyanide solution to a solution of Zinc ions produces a white ppt soluble in sodium hydroxide.

5) Addition of ammonium sulphide solution produces a white precipitate soluble in dilute hydrochloric acid.

6) Using disodium hydrogen phosphate forms white ppt with zinc ions.

Uses of zinc

- Making alloys e.g. Brass is alloy of zinc and copper.
- Galvanizing iron.

Zinc is higher than iron in electrochemical (reactivity) series.

If a galvanized piece of iron developed a small scratch and the iron is exposed, iron does not rust.

This is because the zinc in the neighborhood of the exposed iron undergoes oxidation in preference to iron forming a thin layer of Zinc oxide formed which prevents further attack

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